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## PHOSPHAZENE DIAMINES

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Prepared by:

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16. Abstract  The objectives of this contract were to optimize the synthesis of a specific phosphazene diamine, to prepare other phosphorus-containing diamines, and to evaluate their effect upon certain characteristics of epoxy resins, prepared via reaction with MY 720, in particular, char yield at elevated temperatures.  The synthesis of the phosphazene diamine resulting from the interaction of methylenedianiline with 4,4'-bis(diphenylphosphino)biphenyl was simplified into a one-step process giving 77% yield of the pure product. Using this procedure, a related diamine containing bis(diphenylphosphino) methane was obtained in a 70% yield.  Preparation of another class of phosphorus-containing amines based upon p-aminophenyldiphenylphosphine was unsuccessful; the inability to produce p-aminophenyllithium was responsible for this failure. The approach utilizing amines derived from p-aminophenoxydiphenylphosphine was successfully explored.  Seven epoxy resins employing Araldite MY 720, diaminodiphenylsulfone, and two of the phosphorus-containing diamines were prepared, characterized, and their char yield capacity at elevated temperatures assessed. Based on these investigations, the resins containing phosphorus appear to exhibit significantly better char formation characteristics than materials hardened using conventional amines, without impairing the other properties measured.			
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## FOREWORD

This Final Report describes the work performed by Ultrasystems, Inc. during the period 20 June 1979 through 20 April 1980 under Contract NAS3-22019, "Phosphazene Diamines". The investigations were carried out by K. L. Paciorek, D. H. Harris, T. I. Ito, and R. H. Kratzer, project manager, at the Chemicals and Materials Research Department, Irvine, California. The contract was administered by the NASA Lewis Research Center with Dr. Tito T. Serafini as the project manager.

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## 1. SUMMARY

This is the final report describing work performed by Ultrasystems, Inc. for National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-22019.

The objectives of this contract were to optimize the synthesis of a specific phosphazene diamine, to prepare other phosphorus-containing amines, and to evaluate their effect upon certain characteristics of the resulting epoxy resins, in particular, char yield at elevated temperatures.

The synthesis of the phosphazene diamine,  $H_2N\ddot{P}CH_2\ddot{N}=\ddot{P}(\ddot{\Phi})_2\ddot{\Phi}\ddot{P}-(\ddot{\Phi})_2=N\ddot{P}CH_2\ddot{N}H_2$  (PA), was simplified into a one-step process giving 77% yield of the pure product. Using this procedure, a related diamine,  $H_2N\ddot{P}CH_2-\ddot{N}=\ddot{P}(\ddot{\Phi})_2CH_2\ddot{P}(\ddot{\Phi})_2=N\ddot{P}CH_2\ddot{N}H_2$  (PB), was obtained in a 70% yield.

Preparation of another class of phosphorus-containing amines based upon p-aminophenyldiphenylphosphine was unsuccessful; the inability to produce p-aminophenyllithium was responsible for this failure. The approach utilizing amines derived from p-aminophenoxydiphenylphosphine was successfully explored.

Seven epoxy resins employing Araldite MY 720, diaminodiphenylsulfone, and two of the phosphorus-containing diamines were prepared, characterized, and their char yield capacity at elevated temperatures assessed. Based on these investigations, the resins containing phosphorus appear to exhibit significantly better char formation or yield characteristics than materials hardened using conventional amines, without impairing the other measured properties.

## 2. INTRODUCTION

Phosphorus and nitrogen, especially when contained in aromatic structures or when substituted by aromatic moieties such as phenyl groups, have been shown to form mechanically strong chars [ref. 1,2]. Such chars thermally insulate the lower layers of the polymers thus inhibiting pyrolysis and preventing the access of oxygen to the subsurface. Under Contract NAS3-17829 [ref. 3], it was established that a phosphazene diamine,  $\text{H}_2\text{N}-\text{CH}_2-\text{N}=\text{P}(=\text{O})_2-\text{P}(=\text{O})_2-\text{N}=\text{CH}_2-\text{NH}_2$  (PA), could be used to replace methylene dianiline in the preparation of polyimides. The fiber reinforced laminates thus obtained exhibited greatly increased resistance to burn-through when exposed to a stoichiometric oxygen/natural gas flame as compared to the laminates manufactured using methylene dianiline. To improve the char forming properties of epoxy resins, investigations were undertaken to synthesize several phosphorus-containing diamines. The effects of the phosphazene diamines on resin characteristics were also investigated. Another objective of this program was to simplify and optimize the previously developed synthesis procedure for the phosphazene diamine, PA, described above.

### 3. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Molecular weights (MW) were determined in chloroform solutions using a Mechrolab Osmometer Model 302 at concentrations of 4-6 mg/ml. Infrared (IR) spectra were recorded on double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Differential scanning calorimetry (DSC), differential thermal (DTA), and thermogravimetric analysis (TGA) were performed on a duPont 951/990 Thermal Analyzer.

All materials synthesized were dried in vacuo at appropriate temperatures before physical and chemical characterization. The melting points of the monomers were determined in nitrogen-filled or evacuated sealed capillaries. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

#### Nomenclature

Since both the structural formulae and the appropriate chemical nomenclature for the monomers used during this program are complex and cumbersome, these compounds have been coded to aid in clarity of presentation throughout this report. The codes used are as follows:

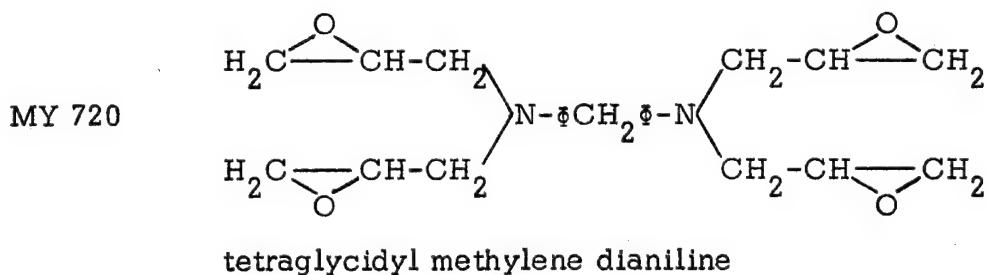
PA            $\text{H}_2\text{N} \ddot{\text{S}} \text{CH}_2 \ddot{\text{S}} \text{N}=\text{P}(\ddot{\text{S}})_2 \ddot{\text{S}} \text{P}(\ddot{\text{S}})_2 =\text{N} \ddot{\text{S}} \text{CH}_2 \ddot{\text{S}} \text{NH}_2$   
bis-aminophosphazene, based on 4,4'-bis(diphenylphosphino)-biphenyl

PB  $\text{H}_2\text{N}\ddot{\text{C}}\text{H}_2\ddot{\text{P}}(\ddot{\text{O}})_2\text{CH}_2\ddot{\text{P}}(\ddot{\text{O}})_2=\text{N}\ddot{\text{C}}\text{H}_2\ddot{\text{N}}\text{H}_2$   
bis-aminophosphazene, based on bis(diphenylphosphino) methane

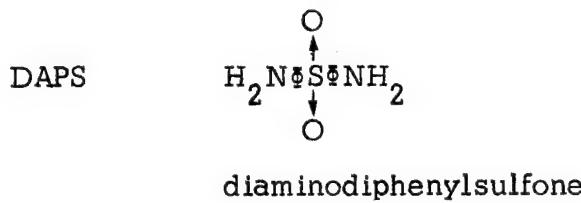
MDA  $\text{H}_2\text{N}\ddot{\text{C}}\text{H}_2\ddot{\text{N}}\text{H}_2$   
4,4'-methylene dianiline

BDBI  $(\ddot{\text{O}})_2\text{P}\ddot{\text{O}}\text{P}(\ddot{\text{O}})_2$   
4,4'-bis(diphenylphosphino) biphenyl

DPPM  $(\ddot{\text{O}})_2\text{PCH}_2\ddot{\text{P}}(\ddot{\text{O}})_2$   
bis(diphenylphosphino) methane



tetraglycidyl methylene dianiline



AN  $\text{H}_2\text{N}\ddot{\text{C}}$   
aniline

Preparation of 4,4'-bis(diphenylphosphino) biphenyl, BDBI

The procedure followed was essentially that of Baldwin and Cheng [ref. 4] with minor modifications in the work-up. All operations were carried out under nitrogen with strict exclusion of oxygen and moisture. To a solution of 4,4'-dibromobiphenyl (74.7 g, 0.24 mol) in freshly distilled dry tetrahydrofuran (250 ml) was added at -70°C over 1.5 hr, a solution of n-butyllithium in hexane (208.7 ml of 2.3M solution). The rate of addition

was regulated to maintain a temperature of less than -65°C. When addition was complete, the reaction mixture was allowed to warm up to 0°C, re-cooled to -70°C, and neat chlorodiphenylphosphine (105.9 g, 86.2 ml, 0.48 mol) added over 2.3 hr. Again the rate of addition was such that a reaction temperature of less than -65°C was always maintained. After warming to room temperature, degassed water-methanol (300 ml, 2:1 mixture) was cautiously added to the milky white suspension resulting in heat and gas evolution. Filtration under nitrogen, followed by further washing with water (600 ml) until a negative halide test indicated all lithium halides had been removed, afforded a slightly sticky white solid. Trituration with methanol (600 ml) at reflux temperature for 1 hr, filtration while hot, followed by drying in vacuo for 24 hr, gave the desired product (99.4 g, 80.0% yield); mp 189-191°C (mp 190-191°C [ref. 4]). IR, <sup>1</sup>H, and <sup>31</sup>P NMR indicated the product to be of high purity (see Figure 1 for <sup>31</sup>P NMR).

#### Purification of 4,4'-methylene dianiline, MDA

Previous work [ref. 3] had indicated that the best solvent system for the recrystallization of MDA was benzene/diethyl ether; however, chlorinated solvents, e.g., CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> admixed with hydrocarbons, e.g., pentane or hexane, have been found to be extremely efficient.

As received, MDA (37.0 g; yellow-orange in color) was readily dissolved in a minimum of dichloromethane (~ 100 ml) and boiled with de-colorizing charcoal. After filtration of the hot solution, hexane was added until the orange solution turned cloudy. The flask was left to stand overnight affording pale tan colored crystals of pure product (34.0 g, 92% recovery) characterized by mp 91-92°C, infrared spectral analysis and <sup>1</sup>H NMR (mp 92-93°C [ref. 5]; see Figure 2 for <sup>1</sup>H NMR).

#### Preparation of phosphazene diamine, PA

A mixture of BDBI (10.46 g, 20.0 mmol), MDA (8.00 g, 40.4 mmol),

triethylamine (5.06 g, 8.33 ml, 60 mmol), and carbon tetrachloride (8.09 g, 5.0 ml, 51.8 mmol) in chloroform (200 ml) was heated at reflux temperature for 42 hr. At the end of this period, the cool orange solution was treated with 200 ml of degassed water. After separation of the organic layer, the aqueous portion was extracted with another 150 ml of chloroform. Removal of the solvent from the combined organic extracts gave a sticky yellow solid which on trituration with diethyl ether (2 x 150 ml) was transformed into a yellow powder (15.1 g, 82.5%). To purify the material further, it was subjected to diethyl ether Soxhlet extraction over a period of 36 hr. The resultant product (14.0 g, 76.5%), mp 133-136°C dec., MW 930, theory 915.07, exhibited a <sup>31</sup>P NMR spectrum (see Figure 3) showing only a trace of a phosphorus-containing impurity. The infrared spectral characteristics of this material were identical with those obtained for the sample prepared previously [ref. 3].

#### Preparation of phosphazene diamine, PB

A mixture of bis(diphenylphosphino) methane (3.83 g, 10 mmol), MDA (3.97 g, 20 mmol), triethylamine (3.64 g, 5.0 ml, 36 mmol), and carbon tetrachloride (3.40 g, 2.1 ml, 22 mmol) in chloroform (~ 200 ml) was heated at reflux temperature for 66 hr. Workup with degassed water (~ 200 ml) gave a quantitative yield of colorless triethylamine hydrochloride (3.0 g, 100%) from the aqueous solution and a buff-colored sticky foam from the chloroform solution. Trituration of the foam with diethyl ether (2 x 90 ml) at room temperature afforded a cream-colored microcrystalline product (5.40 g, 70%); mp 106-108°C dec. The infrared spectrum and <sup>31</sup>P NMR (see Figure 4) were in agreement with the postulated structure. Anal. Calcd. for C<sub>51</sub>H<sub>46</sub>N<sub>4</sub>P<sub>2</sub>: C, 78.84; H, 5.97; N, 7.21; P, 7.97; MW, 776.86. Found: C, 75.05; H, 6.08; N, 6.87; P, 6.32; MW, 727.

#### Attempted preparation of p-aminophenyldiphenylphosphine via p-aminophenyllithium

To a solution of n-butyllithium in hexane (52.2 ml, 0.12 mol) was

added diethyl ether (150 ml) and solid p-bromoaniline (6.88 g, 0.04 mol) at -60°C. After 9 min, a solution of chlorodiphenylphosphine (7.18 ml, 0.04 mol) in diethyl ether (40 ml) was slowly added over 5 min while maintaining the mixture temperature at -60°C. After stirring for a further 10 min at -45°C, the reaction mixture was allowed to warm to room temperature, followed by 1 hr at reflux temperature. Cautious addition of degassed aqueous 10% HCl solution, followed by separation of the aqueous layer and neutralization with 30% aqueous sodium hydroxide solution, afforded a yellow-brown oil. Extraction with diethyl ether and removal of volatiles in vacuo gave unreacted p-bromoaniline, identified by infrared spectroscopy.

The reaction was repeated using a higher temperature and longer reaction time during the initial synthesis of the intermediate p-aminophenyllithium (-50°C to -38°C over 27 min). However, work up again gave only unreacted p-bromoaniline.

In an attempt to determine if any p-aminophenyllithium was being formed, the first step of the overall reaction was repeated under carefully controlled conditions. The reaction mixture temperature was kept at -60°C for the first 12 min as reported by Gilman and Stuckwisch [ref. 6] and then allowed to warm slowly to room temperature. Aliquots were taken every 3 or 4 min, hydrolyzed and subjected to gas chromatography to determine the presence of aniline. In none of the samples could any aniline be identified; the major component was unreacted p-bromoaniline.

#### Preparation of p-aminophenoxydiphenylphosphine

To a freshly prepared sodium sand (2.19 g, 95.2 mmol) in toluene (100 ml) was added, dropwise, an orange solution of p-aminophenol (10.40 g, 95.2 mmol) in tetrahydrofuran (400 ml). No reaction was observed at room temperature; however, at reflux temperature, a blue-purple solid was slowly deposited. After 4 days at reflux temperature, the reaction mixture was allowed to cool to room temperature and a solution of chlorodiphenylphosphine

(17.09 ml, 95.2 mmol) in tetrahydrofuran (50 ml) was added over 15 min. The blue-purple solid and colorless supernatant liquid rapidly changed to a finely divided white solid (presumably NaCl) and a yellow solution, respectively. The mixture was stirred at room temperature for 1.5 hr to complete reaction; the yellow solution was then separated from the white precipitate via syringe, concentrated in vacuo, and diethyl ether added to afford a pale mauve solid (21.2 g, 75.8%). Crystallization of the crude product from dichloromethane-hexane gave ~ 50% recovery of pure p-aminophenoxydiphenylphosphine resulting in an overall yield of 38%. The infrared spectrum supported the postulated structure. Anal. Calcd. for  $C_{18}H_{16}ONP$ : C, 73.72; H, 5.50; N, 4.78; O, 5.45; P, 10.56; MW, 293.29. Found: C, 73.16; H, 5.50; N, 3.77; MW, 320.

Reaction of sodium-p-aminophenoxydiphenylphosphine with dichlorophenylphosphine

To a freshly prepared sodium sand (0.58 g, 25.0 mmol) in toluene (~ 30 ml) was rapidly added an orange-red solution of p-aminophenol (3.27 g, 30 mmol) in tetrahydrofuran (~ 150 ml). The mixture was heated at reflux for 65 hr during which time a purple precipitate was formed. Dropwise addition of a solution of dichlorophenylphosphine (1.70 ml, 12.5 mmol) in tetrahydrofuran (~ 25 ml) over 0.5 hr caused the reaction mixture to change color from purple to brown to yellow-brown; on standing, a pale-brown solid settled out. Filtration gave a yellow-brown filtrate and pale-brown solid (1.0 g) identified as contaminated sodium chloride. Concentration of the filtrate in vacuo, followed by addition of diethyl ether afforded unreacted p-aminophenol (1.85 g, 56.6% recovery) identified by infrared spectroscopy. Further concentration followed by addition of pentane gave a yellow-brown oil, which resisted all crystallization attempts.

Interaction of p-aminophenoxydiphenylphosphine with 2,4-diazido-6-phenyl-s-triazine

In an inert atmosphere enclosure, a solution of 2,4-diazido-6-

phenyl-s-triazine (0.35 g, 1.48 mmol) in tetrahydrofuran (20 ml) was slowly added to a stirred solution of p-aminophenoxydiphenylphosphine (0.87 g, 2.97 mmol) in benzene-tetrahydrofuran (20 ml, 1:1 mixture). Evolution of gas was observed. After stirring at room temperature for 115 hr, evaporation of the solvents in vacuo gave a beige colored solid which on crystallization from dichloromethane-diethyl ether afforded 0.77 g (67.5%), mp 166-168°C dec., of what appeared to be the desired product.

General procedure for epoxy resin preparation using MY 720 and the appropriate amine hardener

The procedure followed was essentially that given by CIBA-GEIGY Corp. [ref. 7]. The required quantity of MY 720 was heated in a beaker at 100°C. After the material became mobile, the appropriate quantity of the amine hardener or hardeners (if several were combined) was added with stirring at 100°C until a homogenous mixture was attained. The viscous product was poured into a mold, gelled at 70°C for 60 hr, then cured at 155°C for 24 hr, and post-cured at 200°C for 8-24 hr. The resins prepared and their characteristics are listed in Table I.

Hydrolytic stability testing

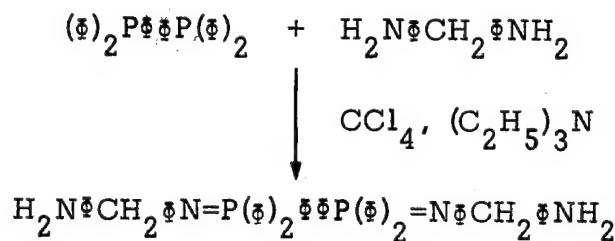
Weighed samples were placed in a desiccator containing an aqueous solution of sodium sulfate (15% by weight) calculated to give a humidity of ~ 95% at 25°C [ref. 8]. The exposure time was 18 days. The weight gain-time relationship is given in Table II.

#### 4. TECHNICAL DISCUSSION

The objectives of this contract were to optimize the synthesis of the phosphazene diamine, PA, originally prepared under a previous contract [ref. 3], to synthesize other phosphorus-containing diamines, and to evaluate the effect of these amine-hardeners upon the properties of MY 720 based epoxy resins. The ultimate aim of the subject program was to increase the char yield of the epoxy resins in oxidizing (air) atmospheres.

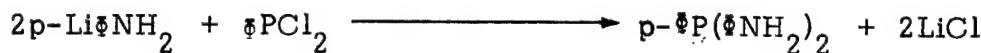
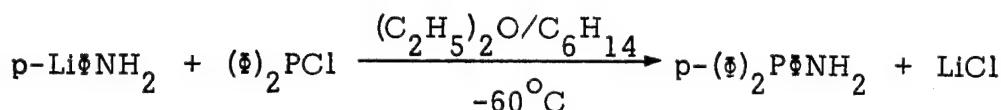
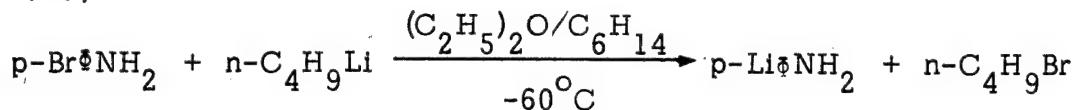
##### 4.1 Monomer Synthesis

PA was prepared previously using the general approach of Appel and coworkers [ref. 9] whereby a phosphonium halide is formed (using carbon tetrachloride as halogenating agent), followed by base dehydrohalogenation, i.e.,



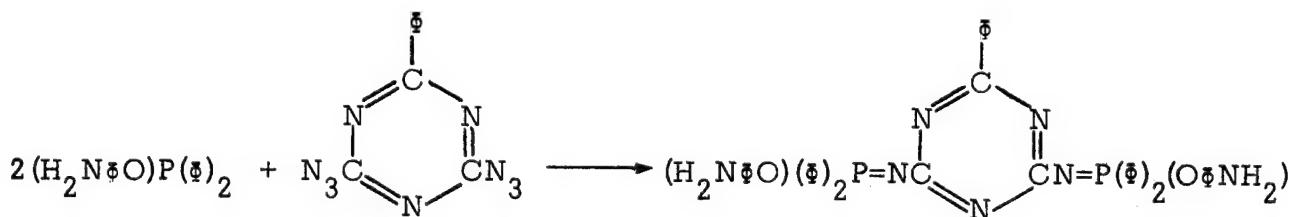
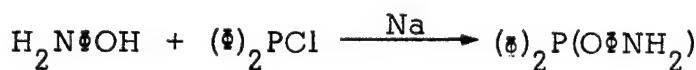
The conditions employed in the early investigations gave only low yields of the desired product; furthermore, the isolation procedures utilized were very tedious. Under the current program, it was established that conducting the reaction, in the presence of an excess of triethylamine, as a one step process in chloroform using a 2:1 diamine to phosphine ratio gave on titration with diethyl ether an 82.5% yield of crude product. Soxhlet extraction with diethyl ether resulted in 76.5% yield of pure PA. This approach was successfully extended into the synthesis of PB,  $H_2 N \ddot{\Phi} CH_2 \ddot{\Phi} N=P(\Phi)_2 CH_2 - P(\Phi)_2 =N \ddot{\Phi} CH_2 \ddot{\Phi} NH_2$ , which was obtained in a 70% yield. It should be noted that both PA and PB on elemental analysis consistently afforded low carbon and phosphorus values due most likely to incomplete combustion.

Another class of phosphorus-containing diamines was expected to be produced from p-bromoaniline via reaction with n-butyllithium followed by treatment with either diphenylchlorophosphine or phenyldichlorophosphine, i.e.,

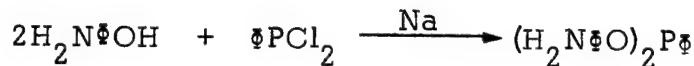


Although the process was reported by Gilman and Stuckwisch [ref. 6], several attempts using various reaction conditions failed to produce the desired p-aminophenyldiphenylphosphine. Furthermore, none of the tests indicated the presence of aniline clearly showing that the initial lithiation of p-bromoaniline did not take place.

In view of this result, other approaches to prepare phosphorus-containing amines were explored. The interaction of p-aminophenol with chlorophosphines was considered to be a promising approach and one that could provide a number of potential hardeners, i.e.,



p-Aminophenoxydiphenylphosphine was obtained in ~ 50% yield from the treatment of sodium p-aminophenoxydiphenylchlorophosphine with diphenylchlorophosphine. The subsequent reaction with 2,4-diazido-6-phenyl-s-triazine appeared to afford the desired product, however, this was not unequivocally established.



The attempted synthesis of bis(p-aminophenoxy) phenyl phosphine was not successful.

#### 4.2 Polymer Investigation

Seven epoxy resins incorporating Araldite MY 720 and varying quantities of DAPS, PA, PB, and AN were prepared and characterized. These resins, together with their properties, are listed in Table I. The inclusion of aniline (AN), a monoamine, in this series was prompted by the synthesis results wherein phosphorus-containing monoamines such as, e.g., p-aminophenoxydiphenylphosphine were obtained and thus their potential applicability as hardeners needed to be tested.

Examining the data given in Table I, it is apparent that the phosphazene diamines afforded definitely faster gelation than, e.g., DAPS; whether this is due to increased reactivity or the higher molecular weight of the segment is unknown. The densities of the resins containing phosphorus were definitely lower than those formed from conventional amines including aniline. The glass transition points for all the resins, with the exception of the material hardened with aniline, were comparable. The same applied to moisture uptake results. The high value reported for 1:1/MY 720:PB must be erroneous based on the values found for the other PB-containing resins. The moisture uptake data with respect to time of exposure are presented in Table II.

Insofar as the effect of phosphorus upon char yield is concerned, it can be seen from the TGA data presented in Table III that under oxidizing conditions, the presence of phosphorus increases the mass retention by a factor ranging between 4 to 15. The most pronounced improvement in the char formation characteristics was exhibited by 2:1/MY 720:PB resin. It should be noted that all of the PB-containing formulations showed the most improved char retention. The exposure of the resins to 95% humidity did not appear to adversely affect the char yield or degradation rate above  $\sim 300^{\circ}\text{C}$ . However, for all of the humidity aged resins the weight loss onset ( $\sim 100\text{-}150^{\circ}\text{C}$  vs.  $\sim 200\text{-}250^{\circ}\text{C}$ ) was significantly lower both in inert and air atmospheres. This could be ascribed to the evaporation of adsorbed moisture. It is noteworthy that in the case of the phosphazene diamine-containing resins, in some instances after the moisture exposure better char yields in inert and oxidizing atmospheres were realized. This is particularly evident for the 1:1/MY 720:PB resin (see Table III). The reason for this finding or its significance are unknown. It is also unexplained why oxidation as manifested by weight gain was observed only for one of the phosphazene diamine, PA, containing formulations (see Figure 26) after exposure to 95% humidity atmosphere.

## 5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are conclusions and recommendations reached during the current investigations of phosphazene diamines as potential candidates in epoxy-resin optimization.

- 1) The synthesis procedure for phosphazene diamine, PA, was optimized to a one-step process yielding 77% of pure product without the need for extensive purification.
- 2) The related phosphazene diamine, PB, was synthesized in 70% yield.
- 3) The presence of the phosphazenes in epoxy resins appears to impart better char forming characteristics, particularly under aerobic conditions, than is the case with conventional hardeners.
- 4) Other phosphorus-containing amine classes were only briefly investigated; preliminary results appear promising. Further study is necessary to assess their actual suitability as epoxy resin hardeners.

## 6. REFERENCES

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8. International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Company, Inc., New York, 1928, pg. 371.
9. R. Appel, *Angew. Chem.*, 87, 863 (1975) and references cited therein.

TABLE I  
EPOXY RESINS CHARACTERIZATION DATA

Resin	Gelation hr	D <sub>25°C</sub> g/ml	T <sub>g</sub> <sup>a</sup> °C	Moisture Uptake %
1:1/MY 720 : DAPS	52	1.34	210	2.18
1:1/MY 720 : PA	1.5	1.11	200	2.25
2:1:1/MY 720 : DAPS : PA	n.d. <sup>c</sup>	1.16	200	1.90
1:1/MY 720 : PB	1.5	0.94	260	2.92
2:1/MY 720 : PB	n.d.	1.10	240	2.19
7:5:2/MY 720 : DAPS : PB	<15	1.15	210	1.84
1:2/MY 720 : AN	5	1.26	135	0.49 <sup>d</sup>

- a) The glass transition temperatures were determined using a DTA technique.
- b) This is the saturation value obtained after equilibration in 95% humidity chamber for 18 days.
- c) Not determined.
- d) This value was obtained after 15 days.

TABLE II  
WEIGHT GAIN OF FULLY CURED RESINS  
ON EXPOSURE TO 95% HUMIDITY<sup>a</sup>

Sample	Weight Percent Gain							
	Day 1	Day 4	Day 6	Day 8	Day 11	Day 13	Day 15	Day 18
1:1/MY 720 : DAPS	0.46	1.05	1.25	1.42	1.71	1.83	1.98	2.18
1:1/MY 720 : PA	0.95	1.63	1.77	1.89	2.01	2.04	2.15	2.25
2:1:1/MY 720 : DAPS : PA	0.60	1.14	1.27	1.43	1.58	1.65	1.74	1.90
1:1/MY 720 : PB	0.97	1.65	1.82	2.04	2.30	2.50	2.66	2.92
2:1/MY 720 : PB	0.81	1.42	1.58	1.74	1.95	2.03	2.07	2.19
7:5:2/MY 720 : DAPS : PB	0.43	0.89	1.01	1.23	1.44	1.54	1.66	1.84
1:2/MY 720 : AN	0.11	0.30	0.30	0.38	0.46	0.46	0.49	n.d.

a) In these tests, 250-350 mg samples were exposed to 95% humidity for the denoted periods of time.

TABLE III  
CHAR FORMATION EVALUATION

Resin	% Char Yield at 700°C					
	Sample Content <sup>a</sup>		Post Cured Samples		After Exposure to 95% Humidity	
	% P	% N	Anaerobic	Air	Anaerobic	Air
1.6:1/MY 720:DAPS <sup>b</sup>	0.0	10.9	32	1.2	n.d.	n.d.
1:1/MY 720:DAPS	0.0	8.4	31	1.3	31	1.3
1:1/MY 720:PA	4.6	6.3	20	6	26	6
2:1:1/MY 720:DAPS:PA	3.1	7.0	30	5	29	9
1:1/MY 720:PB	5.2	7.0	26	12	30	20
2:1/MY 720:PB	3.8	6.9	31	18	30	16
7:5:2/MY 720:DAPS:PB	2.2	7.8	30	9	29	8
1:2/MY 720:AN	0.0	9.2	20	1.5	21	1.3

a) Based on the ingredients used.  
 b) This formulation is based on recommendations of CIBA GEIGY [ref. 7].

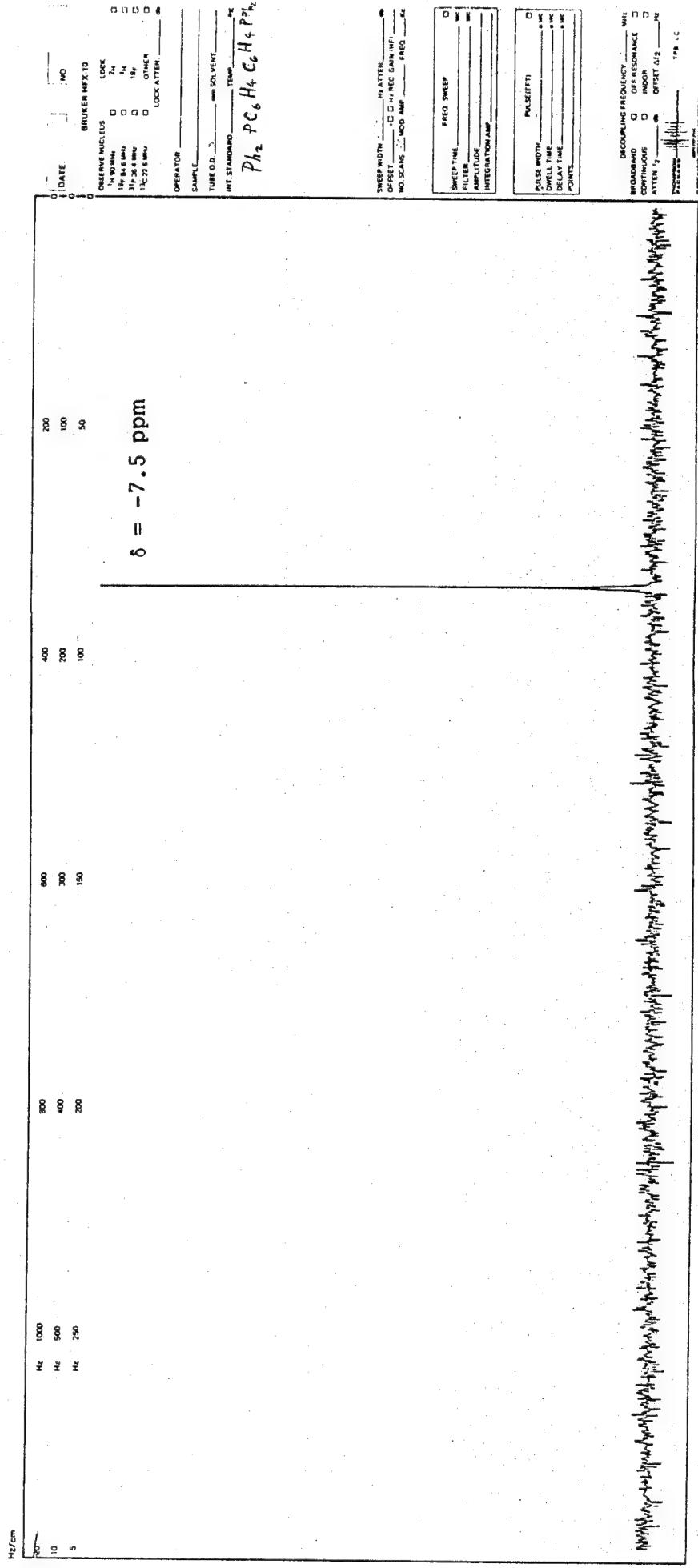


Figure 1:  $^{31}\text{P}$  NMR spectrum of 4,4'-bis(diphenylphosphino) biphenyl, BDBI (external reference 85% ortho-phosphoric acid; 0.00 ppm)

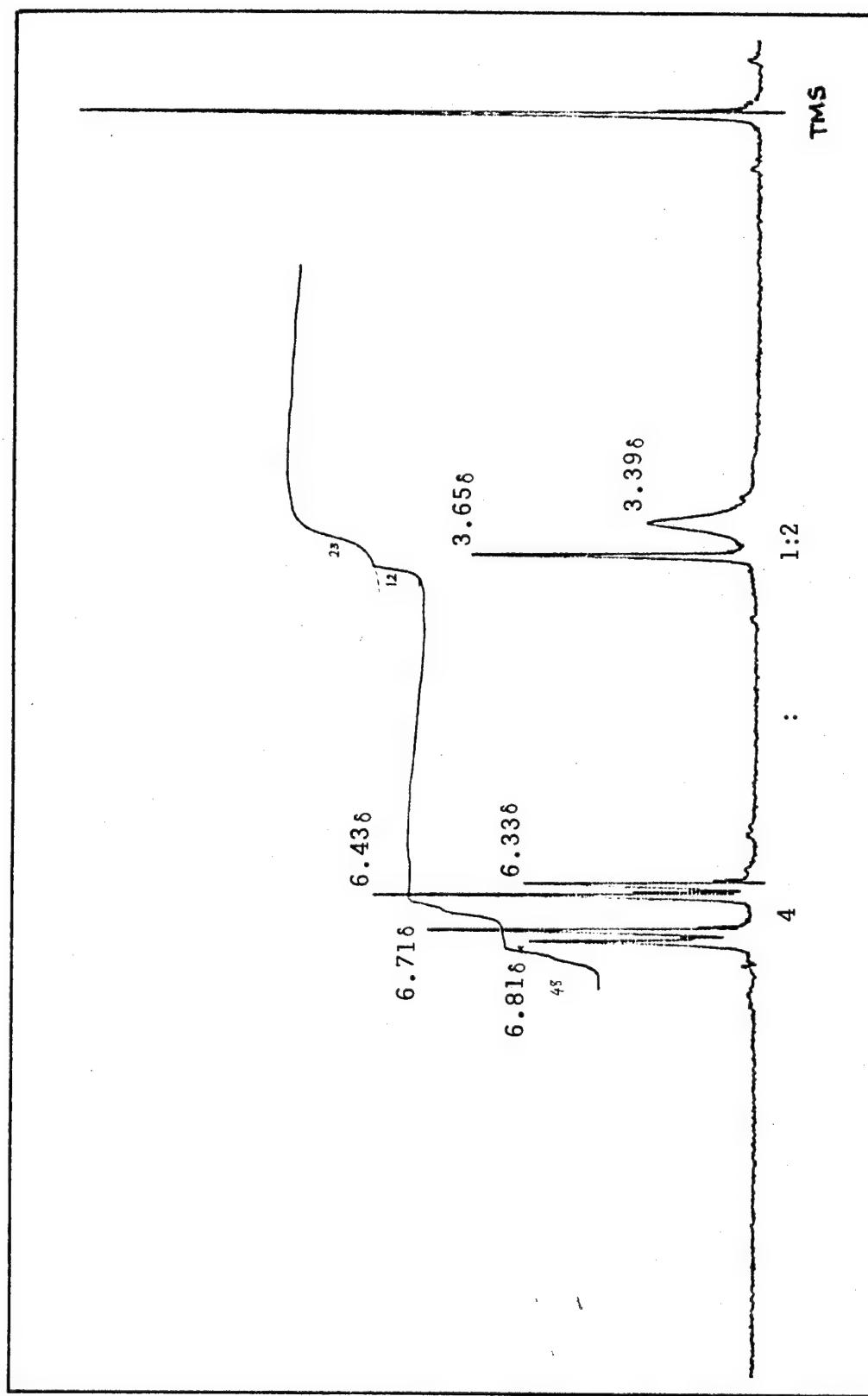


Figure 2:  ${}^1\text{H}$  NMR spectrum of 4,4'-methylenedianiline, MDA (internal reference TMS at 0.00 ppm)

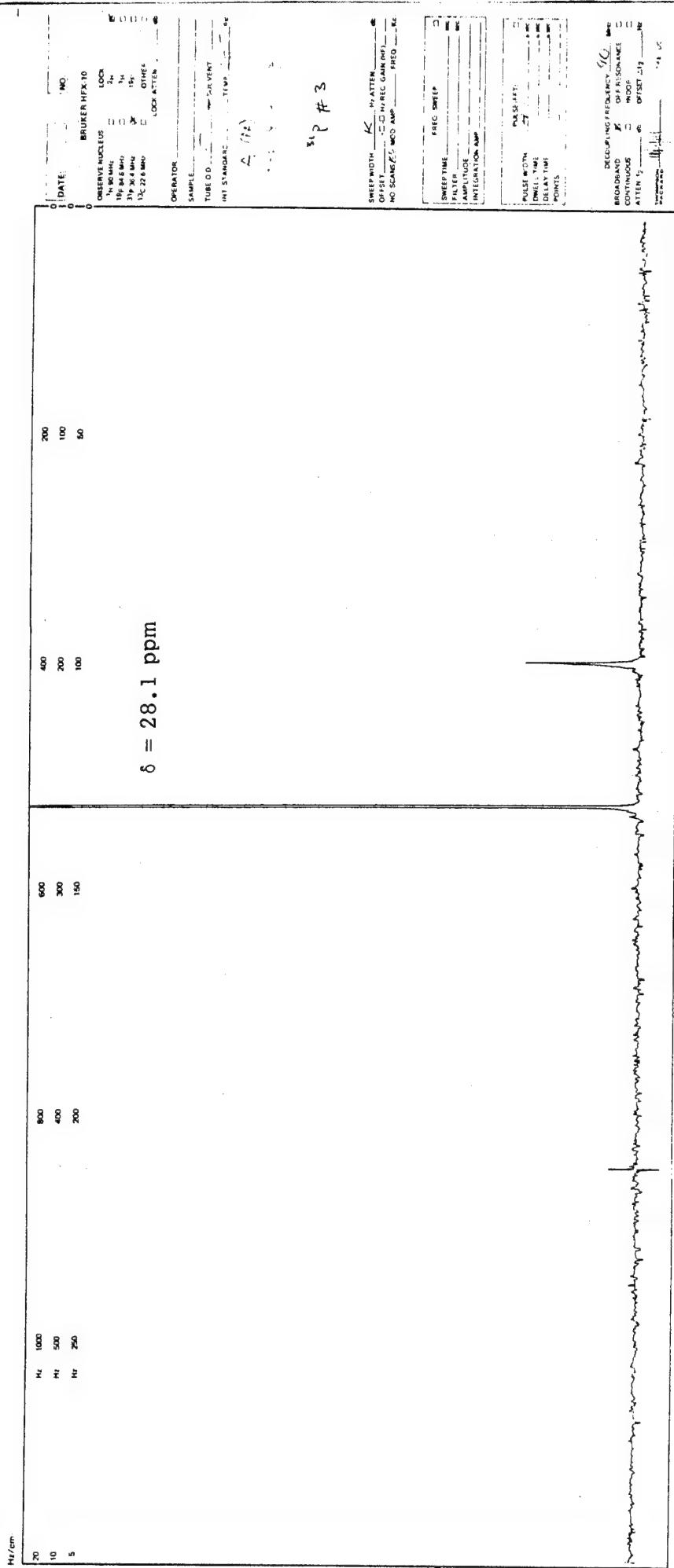


Figure 3:  $^{31}\text{P}$  NMR spectrum of PA in  $\text{CDCl}_3$  solution (external reference 85% ortho-phosphoric acid, 0.00 ppm)

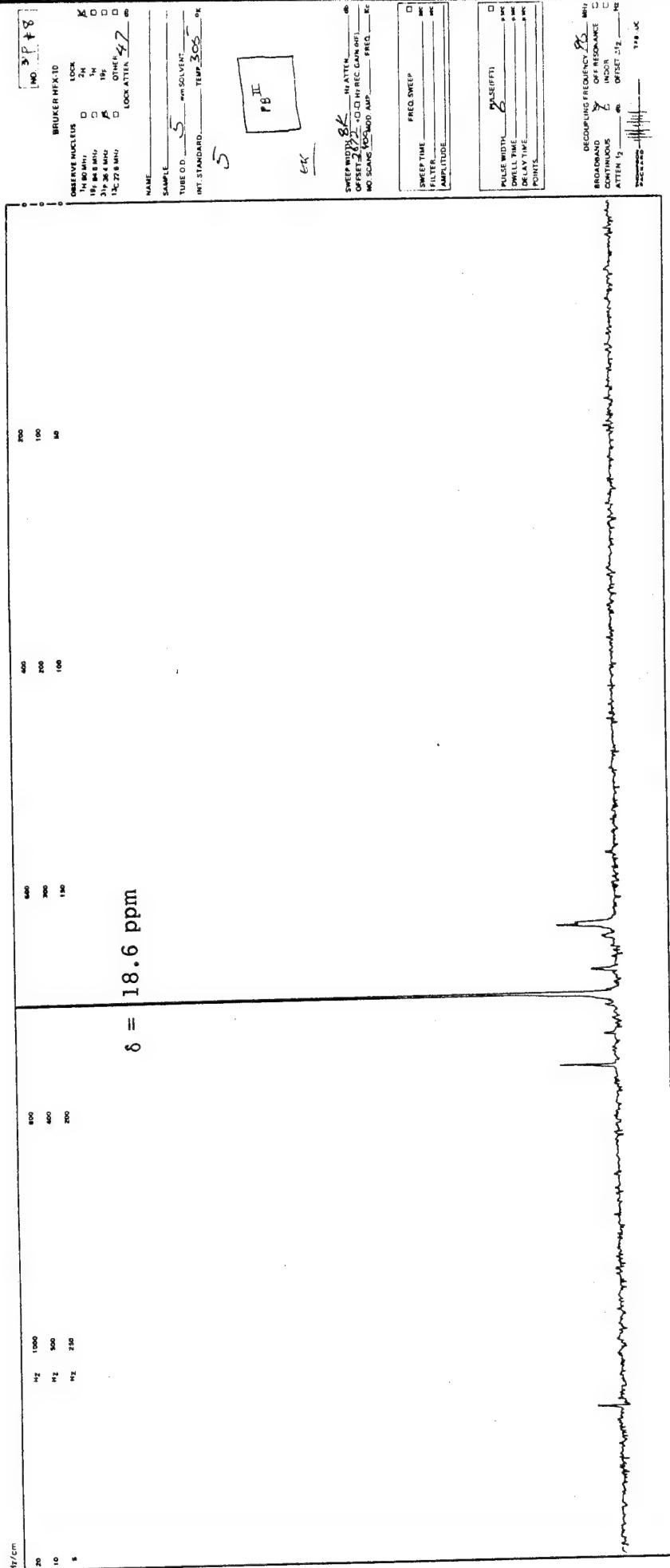


Figure 4:  $^{31}\text{P}$  NMR spectrum of PB in  $\text{CDCl}_3$  solution (external reference 85% ortho-phosphoric acid, 0.00 ppm)

PART NO. 990088	EPOXY RESIN			
	TGA	TMA	ORIGIN	NY 420
RUN NO 469 DATE 25&179	DTA-DSC	SCALE, mils/in	SCALE, mg/in	and p-anisophenyl sulfide
OPERATOR Jm	SCALE, °C/min 50	SUPPRESSION, mg	MODE	
SAMPLE:	PROG. RATE, °C/min 5 HEAT COOL ISO	WEIGHT, mg	SAMPLE SIZE	
ATM N <sub>2</sub> @ 100 ml/min	SHIFT, in 0	TIME CONST., sec 1	LOAD, g	
FLOW RATE	REFERENCE	dy. (10X) /in 0.2	dY. (mils/min) /in	

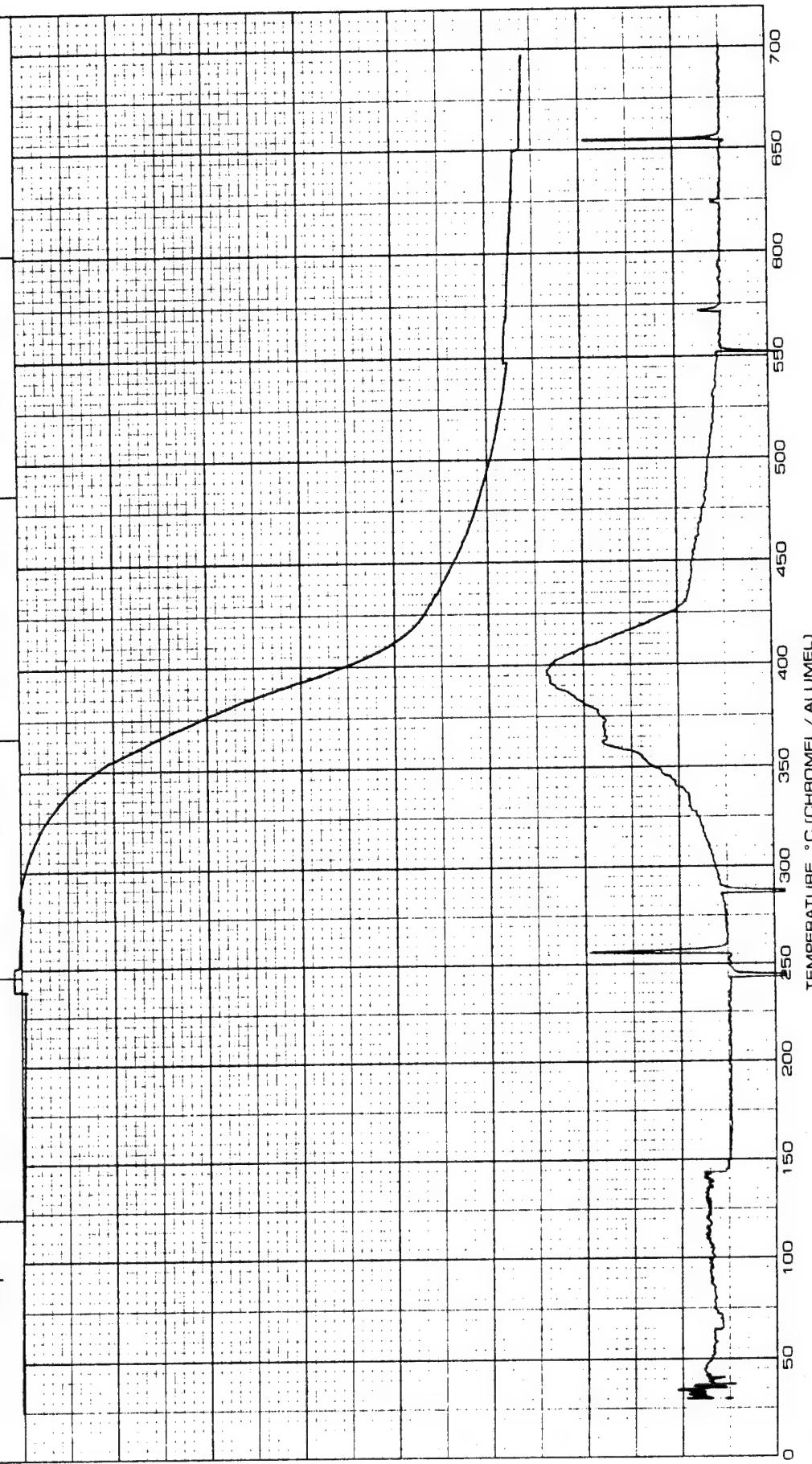


Figure 5: TGA of epoxy resin formed from 1.6:1 stoichiometric mixture of MY 720 and DAPS (in nitrogen)

PART NO. 990088

RUN NO. 468 DATE 25/07/91		T-AXIS SCALE, °C/in 50	DSC SCALE, °C/in 50	TGA SCALE, mg/in	TMA SCALE, mils/in	EPOXY RESIN
OPERATOR <i>JM</i>	SAMPLE	PROG. RATE, °C/min 5	(mcal/sec)/in	SUPPRESSION, mg	MODE	
ATM AIR	@	HEAT <input checked="" type="checkbox"/> COOL <input type="checkbox"/> ISO	WEIGHT, mg 10.41	WEIGHT, mg 10.41	SAMPLE SIZE	
FLOW RATE 100 ml/min		SHIFT, in 0	REFERENCE	TIME CONST., sec. 1	LOAD, g	
				dY (10X) (mils/min)/in		
				0.2		

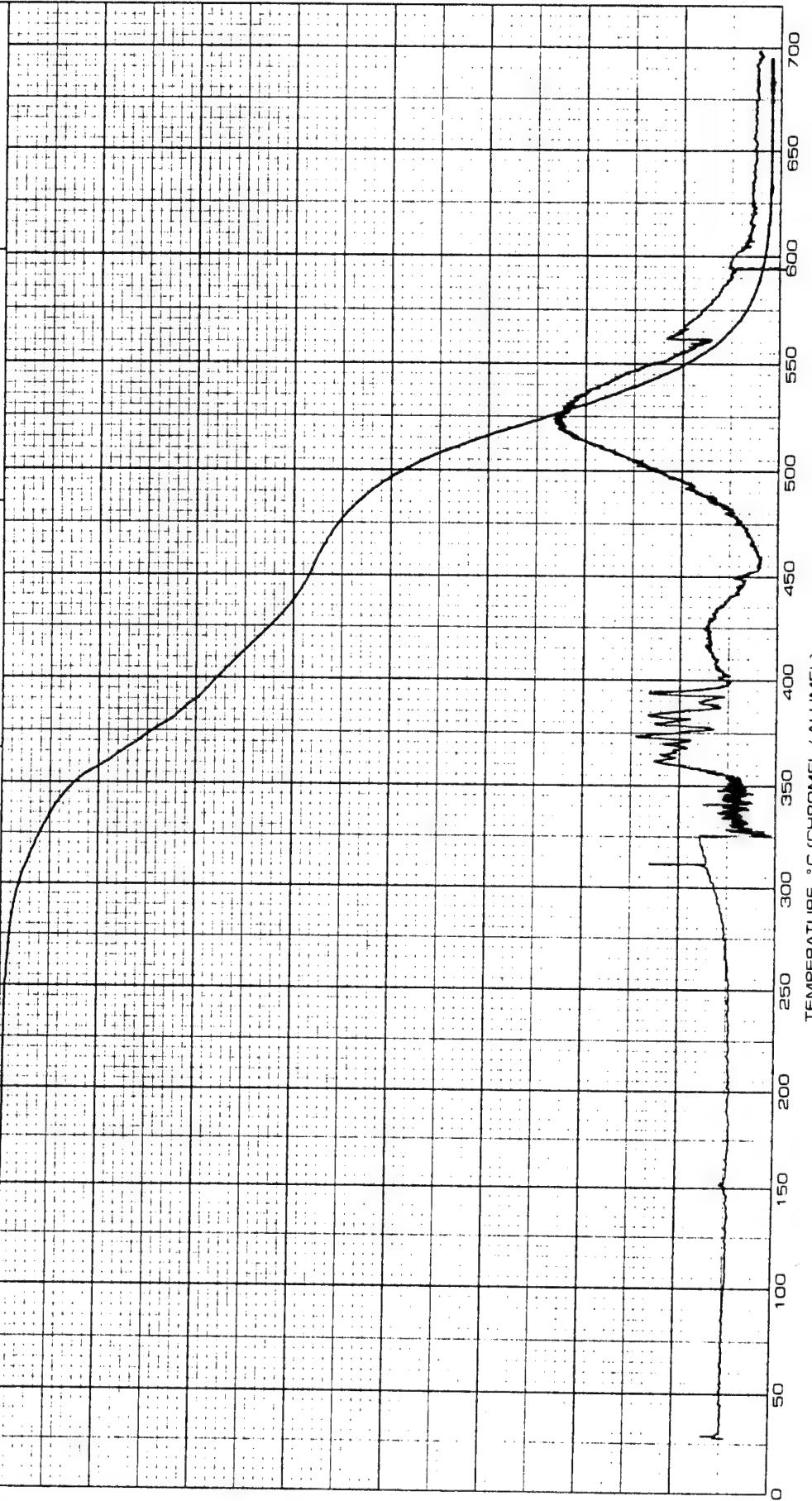


Figure 6: TGA of epoxy resin formed from 1.6 : 1 stoichiometric mixture of MY 720 and DAPS (in air)

PART NO. 999088

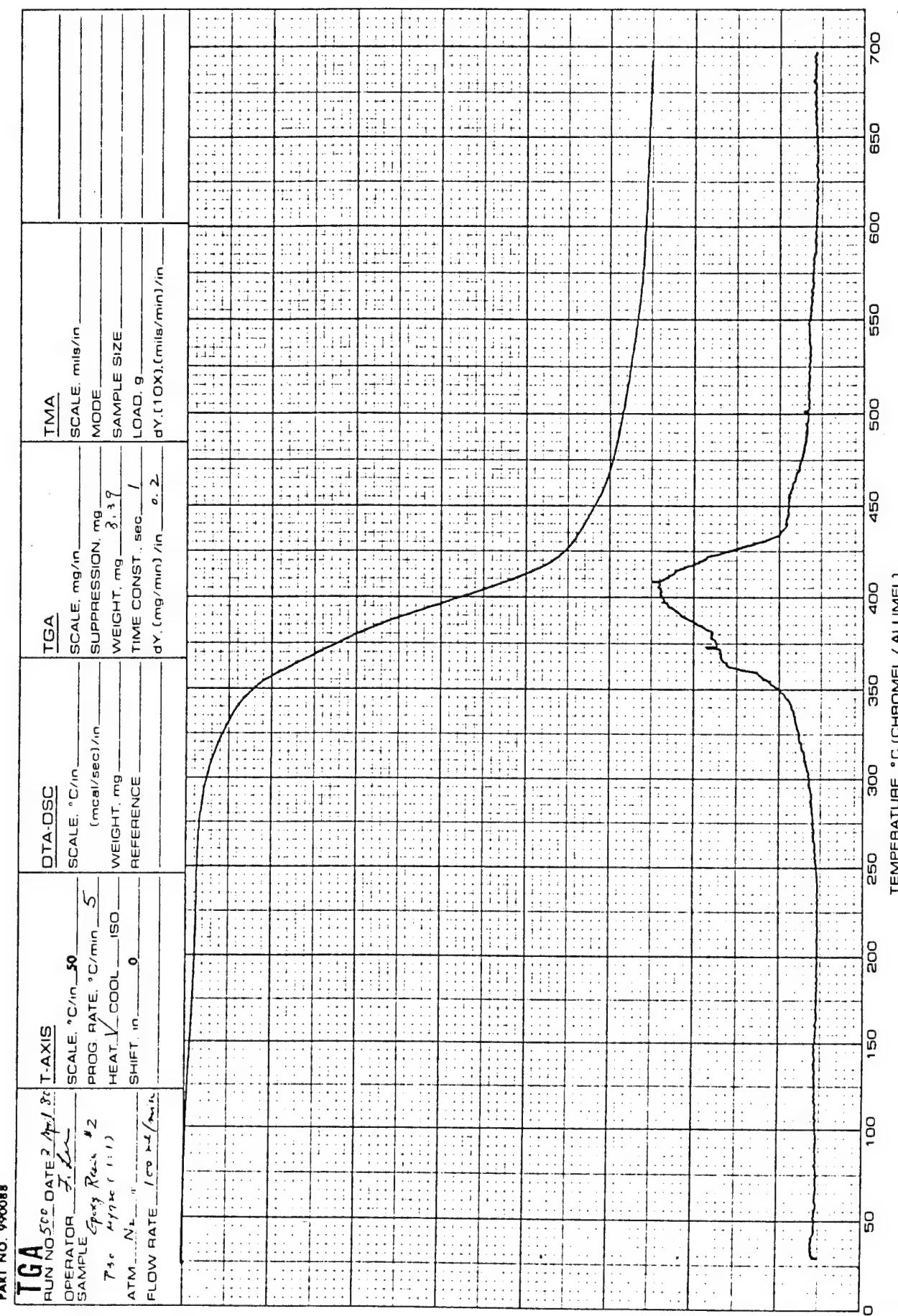


Figure 7: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and DAPS (in nitrogen)

PART NO. 990088

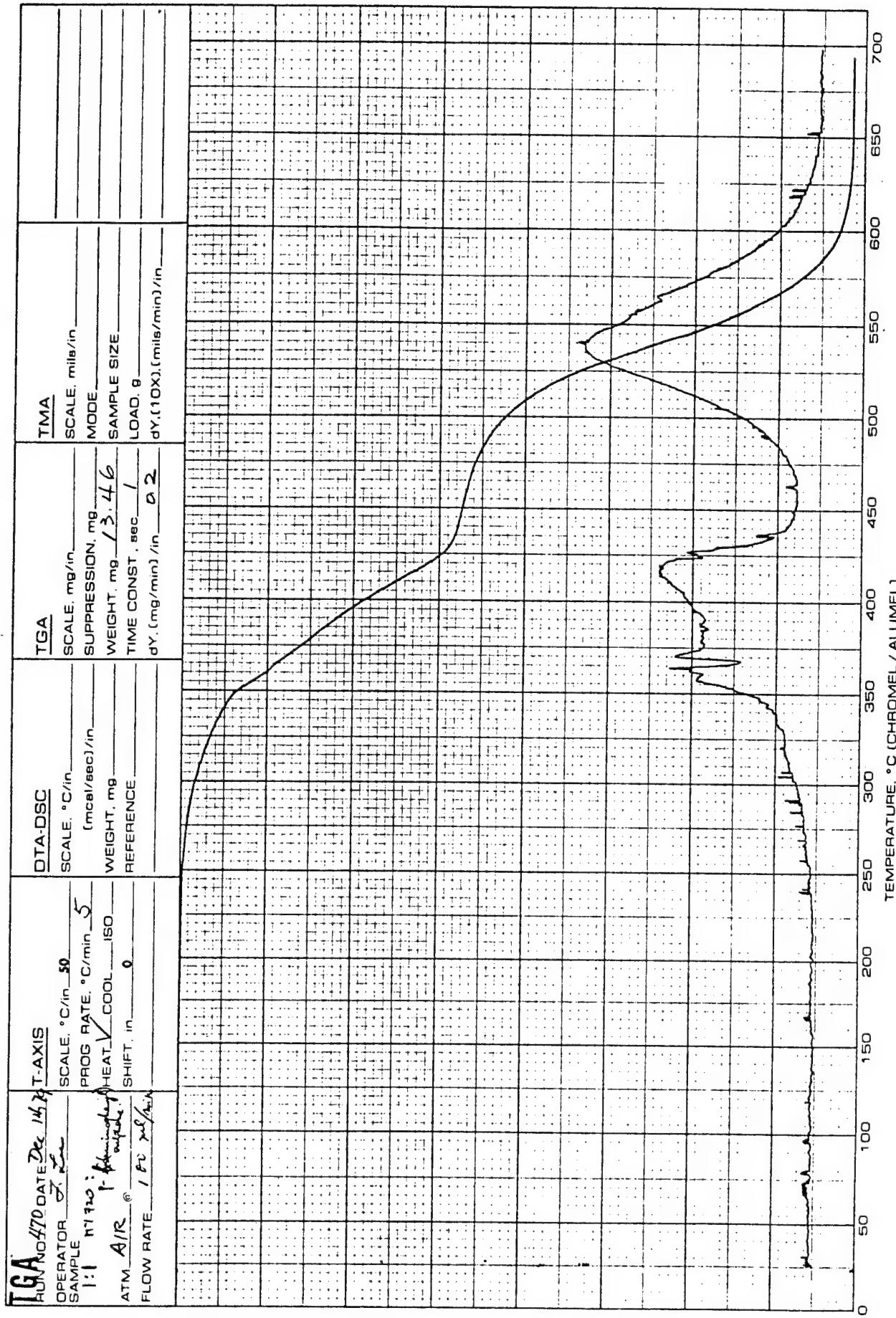


Figure 8: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and DAPS (in air)

# TGA

PART NO. 990088

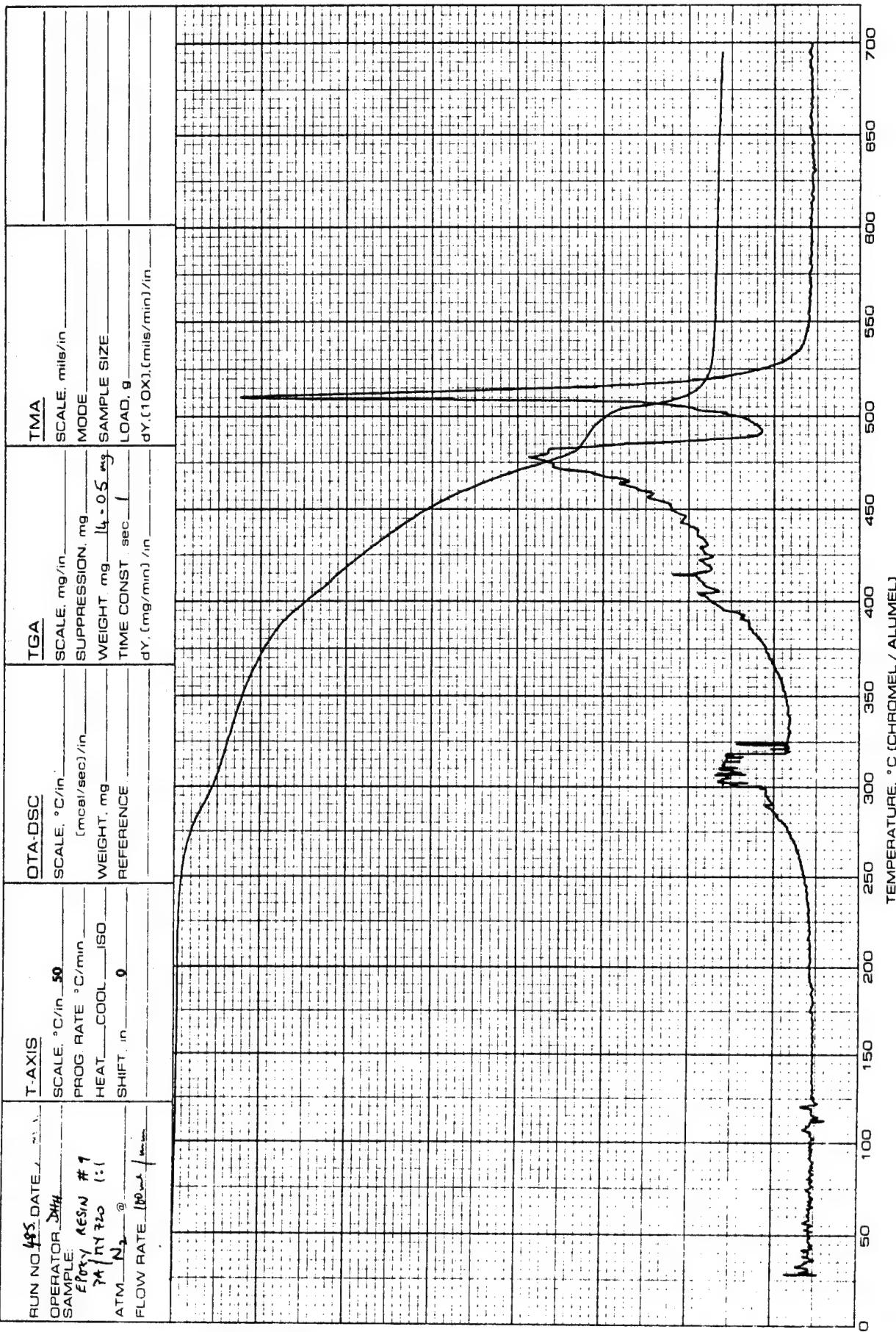


Figure 9: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PA (in nitrogen)

TGA

PART NO. 990088

T-AXIS		DTA-OSC		TGA		TMA	
SCALE °C/in	50	SCALE °C/in	(mcal/sec)/in	SCALE mg/in		SCALE mils/in	
PROG. RATE °C/min		HEAT COOL ISO		SUPPRESSION mg		MODE	
HEAT		COOL		WEIGHT mg	12.25	SAMPLE SIZE	
SHIFT .in	0	REFERENCE		TIME CONST. sec	1	LOAD g	
ATM	412			dY (mg/min)/in		dY (10X) (mils/min)/in	
FLOW RATE	75						

TEMPERATURE °C (CHROMEL / ALUMEL)

Figure 10: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PA (in air)

PART NO. 990088

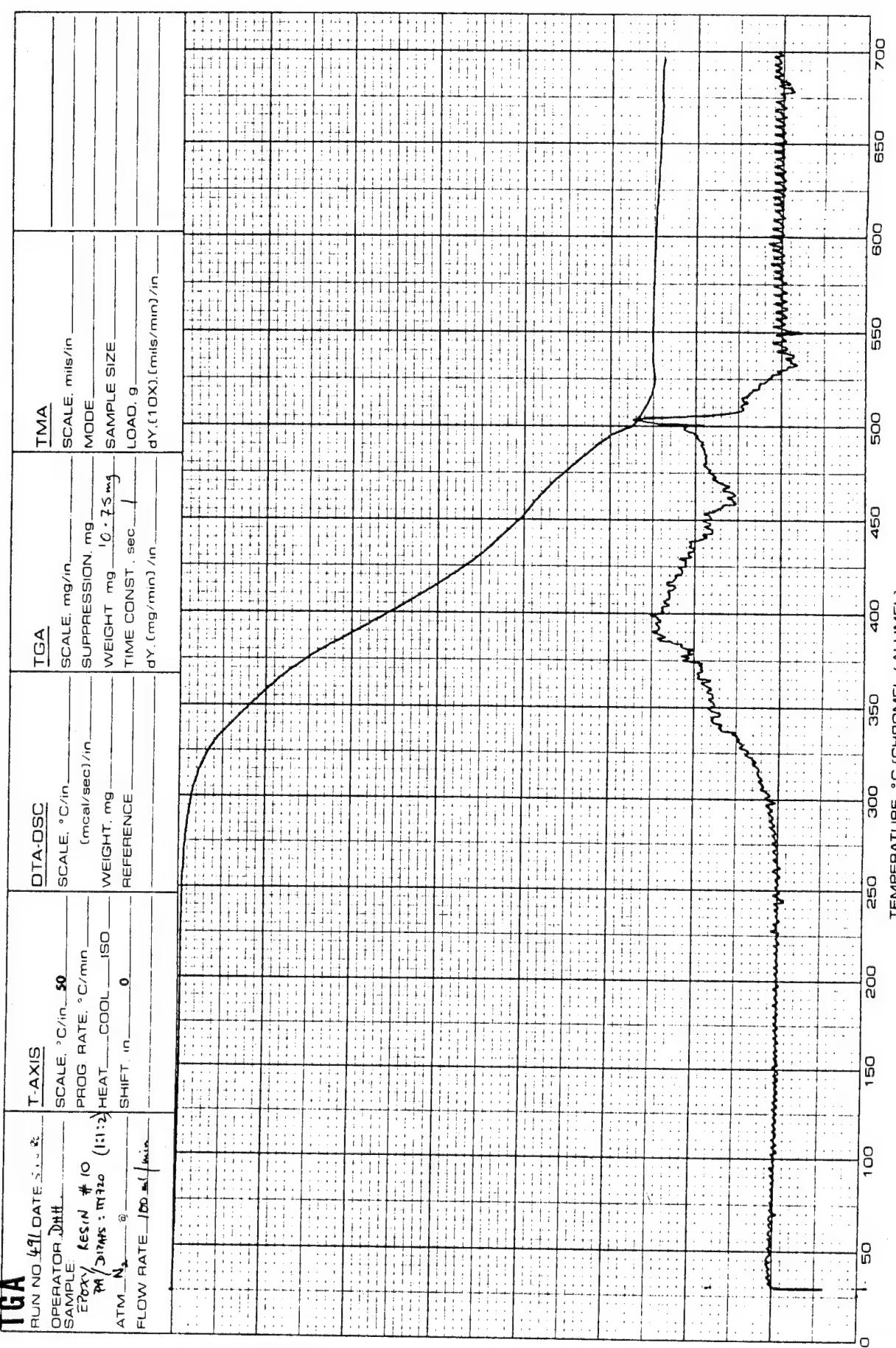
**TGA**

Figure 11: TGA of epoxy resin formed from 2:1 stoichiometric mixture of MY 720, DAPS, and PA (in nitrogen)

PART NO. 990088

**TGA**

RUN NO. 40 DATE 1/26  
 OPERATOR J.W.  
 SAMPLE EPOXY RESIN # 10  
 PA : DAPS : MY 720 / 1:1:2  
 ATM. AIR  
 FLOW RATE 100 ml/min

T-AXIS

SCALE °C/in.

50

PROG. RATE. °C/min.

(mcal/sec)/in.

10

HEAT COOL

1:1:2

SHIFT in.

0

REFERENCE

REFERENCE

DSC

SCALE °C/in.

50

(mcal/sec)/in.

10

WEIGHT mg

11.01

TIME CONST sec

1

dY (10X) (mils/min)/in.

TGA

SCALE mg/in.

50

SUPPRESSION mg

10

LOAD g

9

SAMPLE SIZE

11.01

TEST

LOAD 9

TEST

PART NO. 990088

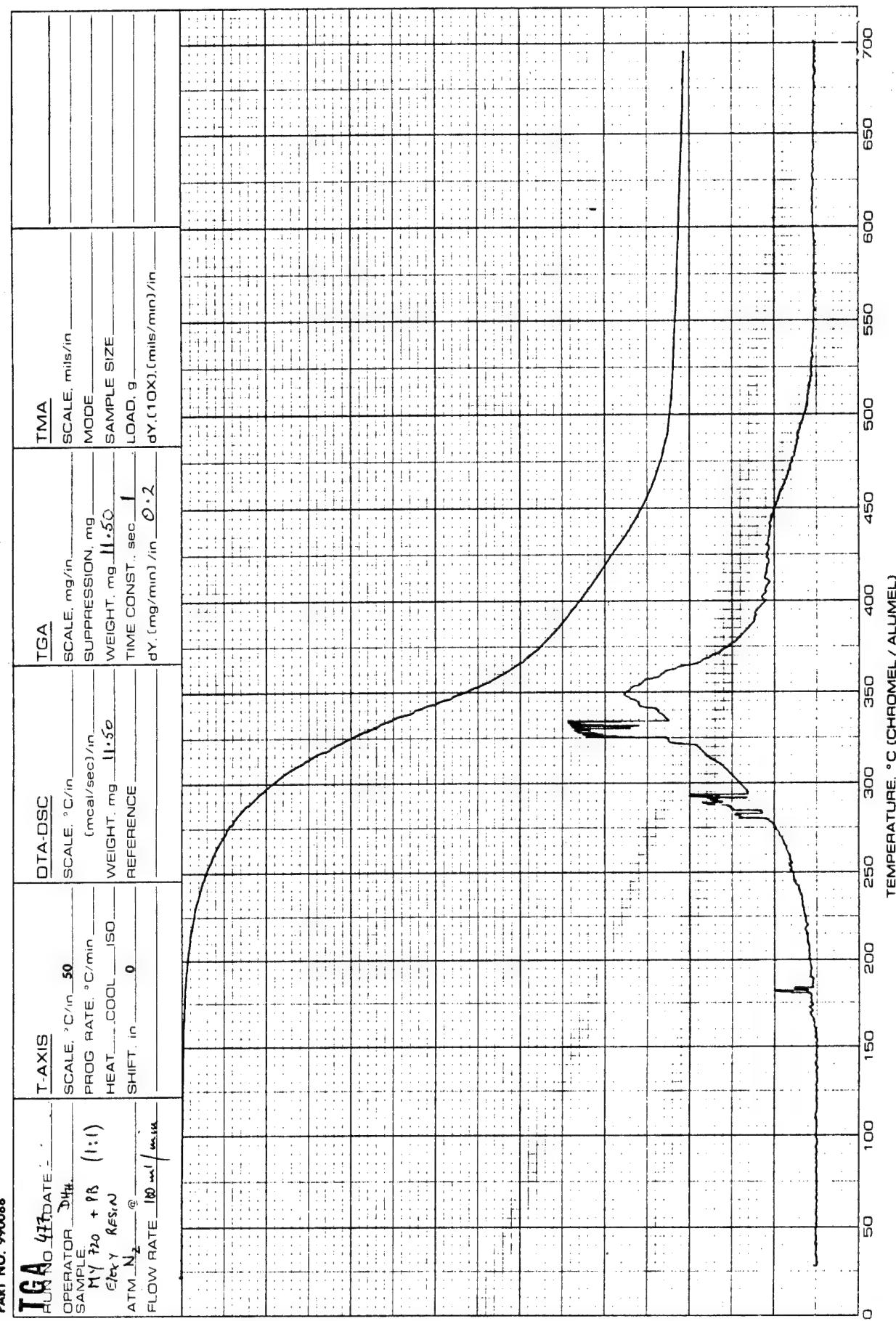


Figure 13: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PB (in nitrogen)

PART NO. 990088

TGA	T-AXIS		DTA-OSC		TGA		TMA	
	SCALE. °C/in	SCALE. °C/min	SCALE. °C/in	(mcal/sec)/in	SCALE. mg/in	SUPPRESSION, mg	SCALE. mils/in	MODE
RUN NO 435 DATE 7/14/66	50	50	PROG RATE. °C/min	10	WEIGHT, mg	12.18	SAMPLE SIZE	
OPERATOR <u>SH</u> F.F.			HEAT COOL ISO		REFERENCE		LOAD, g	
SAMPLE <u>MY 720 + P3</u>	1:1 EPOXY RESIN		SHIFT, in	0				
ATM <u>14R</u>	100 ml / hr		FLOW RATE					

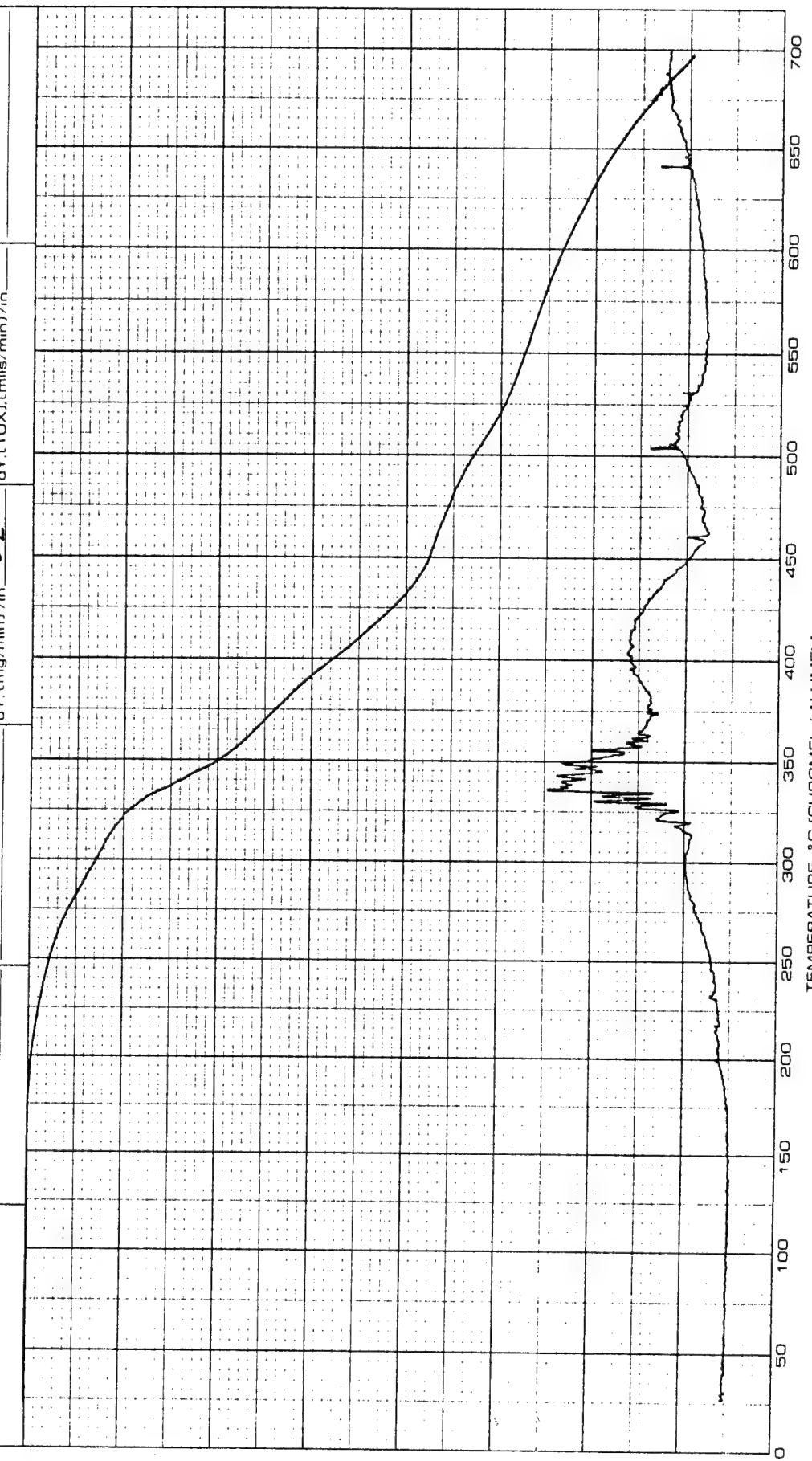


Figure 14: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PB (in air)

# TGA

PART NO. 990086

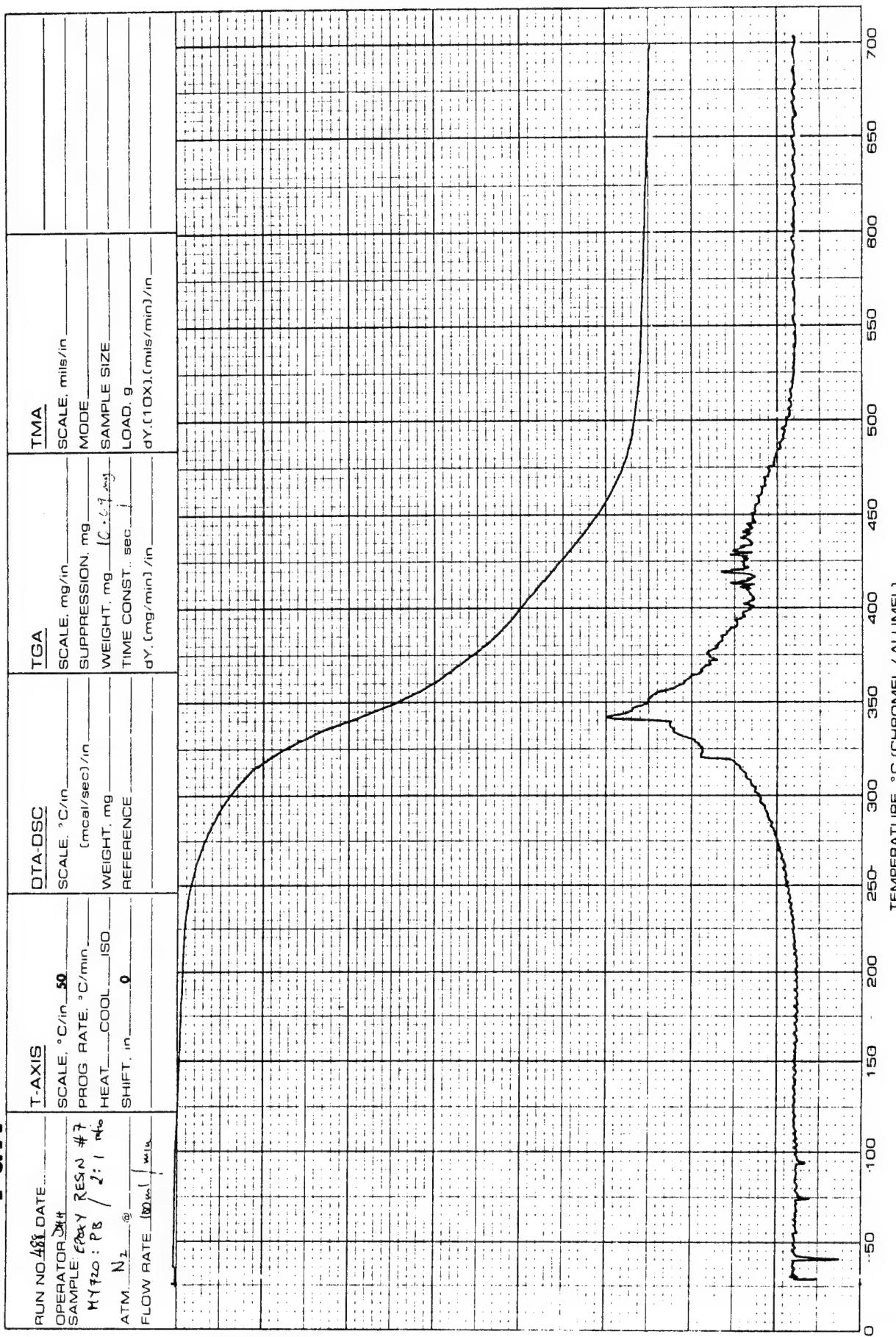


Figure 15: TGA of epoxy resin formed from 2 : 1 stoichiometric mixture of MY 720 and PB (in nitrogen)

TGA

PART NO. 990088

T-AXIS		DTA-DSC		TGA		TMA							
RUN NO	422 DATE	SCALE, °C/in	SCALE, °C/in	SCALE, mg/in	SCALE, mils/in	SCALE, mils/in	SCALE, mils/in						
OPERATOR	DHH	50	(mils/sec)/in	SUPPRESSION, mg	MODE								
SAMPLE	Epoxy Resin #7	PROG. RATE, °C/min	WEIGHT, mg	WEIGHT, mg	SAMPLE SIZE								
	2:1	73	12.14	12.14	LOAD, g								
ATM	AIR	HEAT COOL	REFERENCE	TIME CONST., sec									
	@	ISO		1									
FLOW RATE	180 ml/min	SHIFT, in	dY, (10X), (mils/min)/in										
TEMPERATURE, °C (RANGE) / ALUMEL 1													
50	100	150	200	250	300	350	400	450	500	550	600	650	700

Figure 16: TGA of epoxy resin formed from 2 : 1 stoichiometric mixture of MY 720 and PB (in air)

# TGA

PART NO. 990088

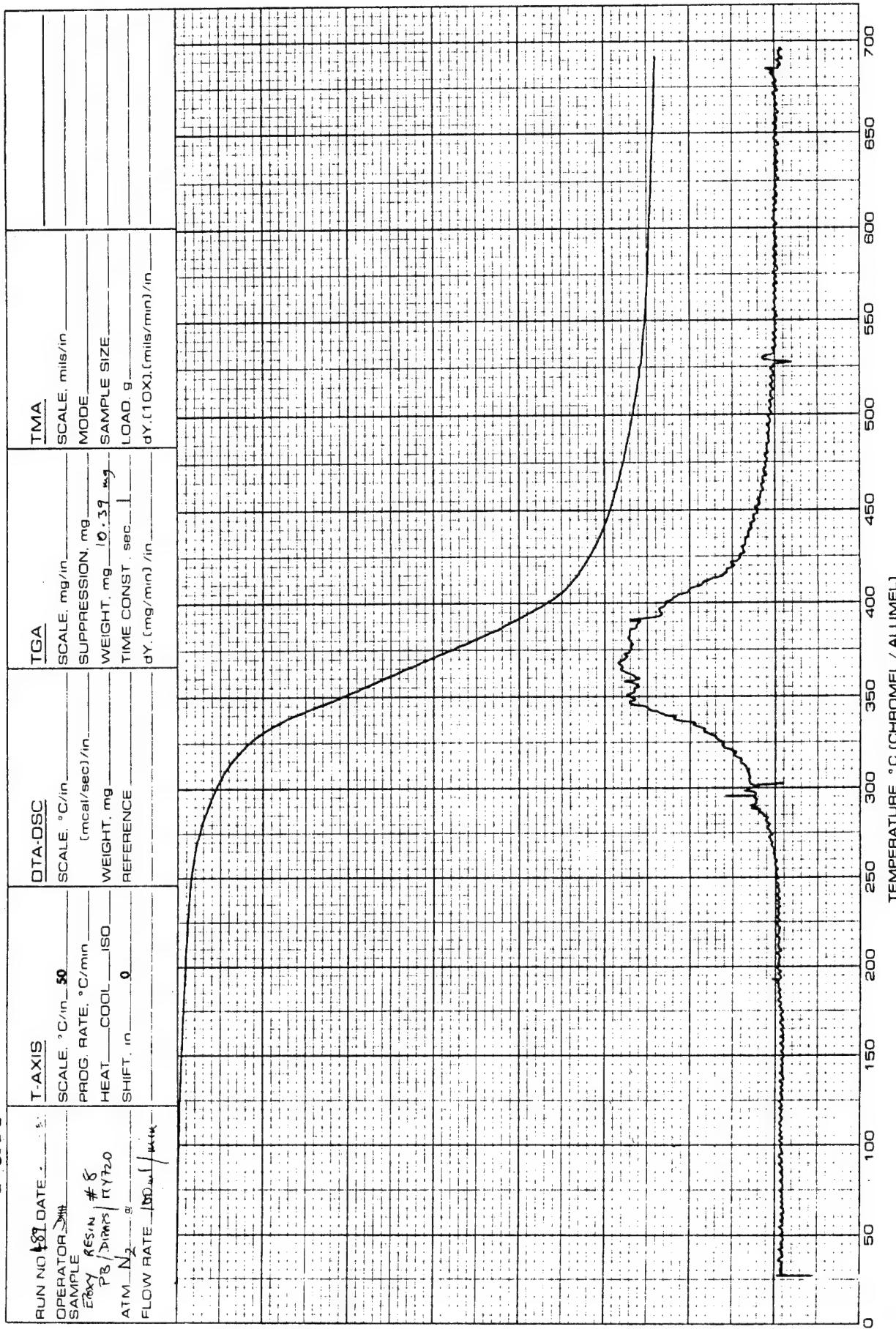


Figure 17: TGA of epoxy resin formed from 7:5:2 stoichiometric mixture of MY 720, DAPS, and PB (In nitrogen)

A  
G  
T

PART NO 990088

RUN NO	DATE	T-Axis	OTA-DSC	TGA	TMA
483	5/15/81	SCALE. °C/in .50	SCALE. °C/in	SCALE. mg/in	SCALE. mils/in
OPERATOR JHH		SCALE. °C/in .50	(mcal/sec)/in	SUPPRESSION, mg	MODE
SAMPLE EPOXY RESIN # 8		PROG. RATE. °C/min	1.68	WEIGHT, mg 11.68	SAMPLE SIZE
PS, DPPH: RT/20		HEAT COOL ISO	WEIGHT, mg 11.68	TIME CONST. sec 1	LOAD, g
ATM AIR	@	SHIFT, in 0	REFERENCE	dY (mg/min)/in	dY. (10X).(mils/min)/in
FLOW RATE 100 ml/min					

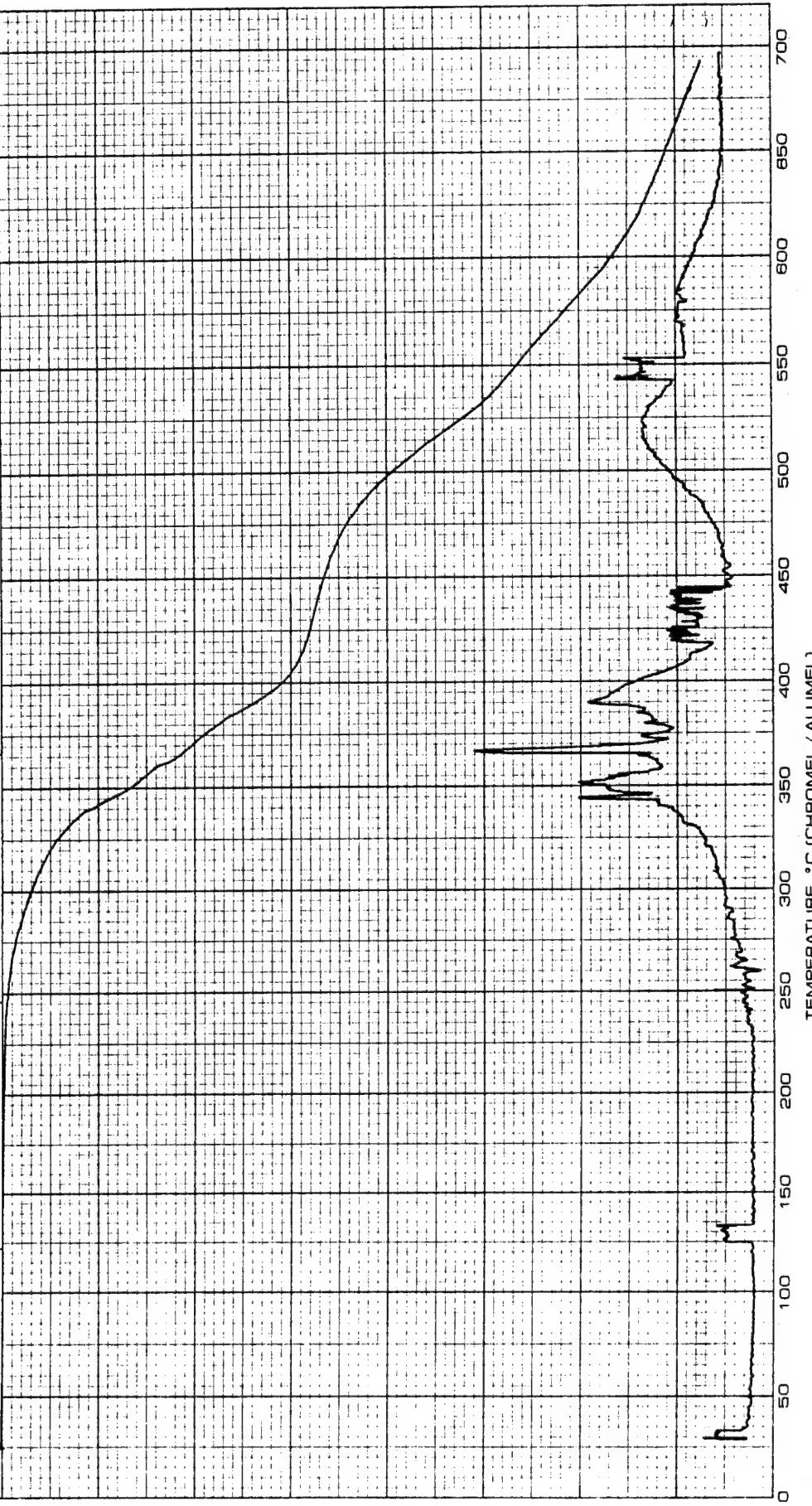


Figure 18: TGA of epoxy resin formed from 7:5:2 stoichiometric mixture of MY 720, DAPS, and PB (in air)

PART NO. 9900088

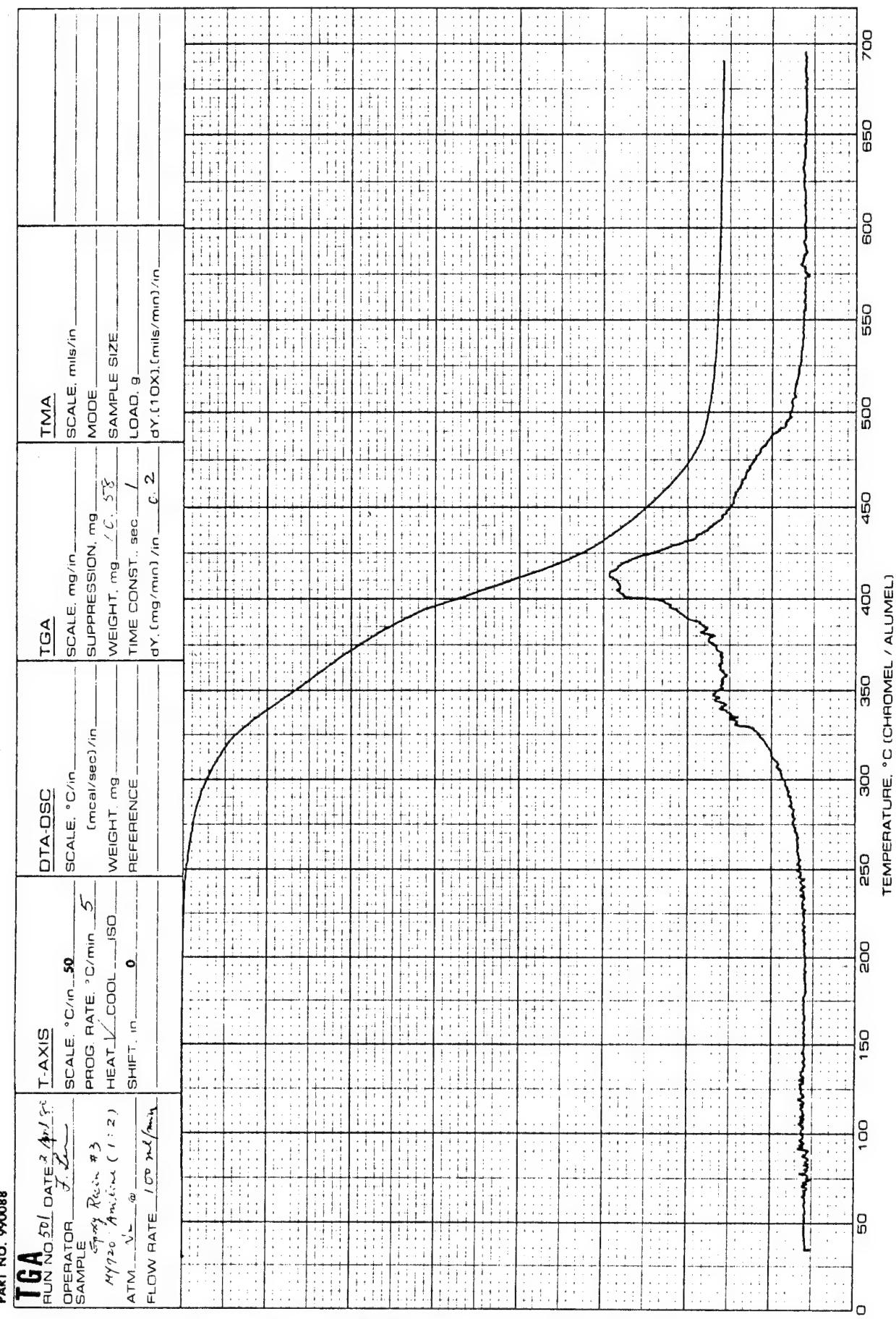


Figure 19: TGA of epoxy resin formed from 1:2 stoichiometric mixture of MY 720 and AN (in nitrogen)

PART NO. 990088

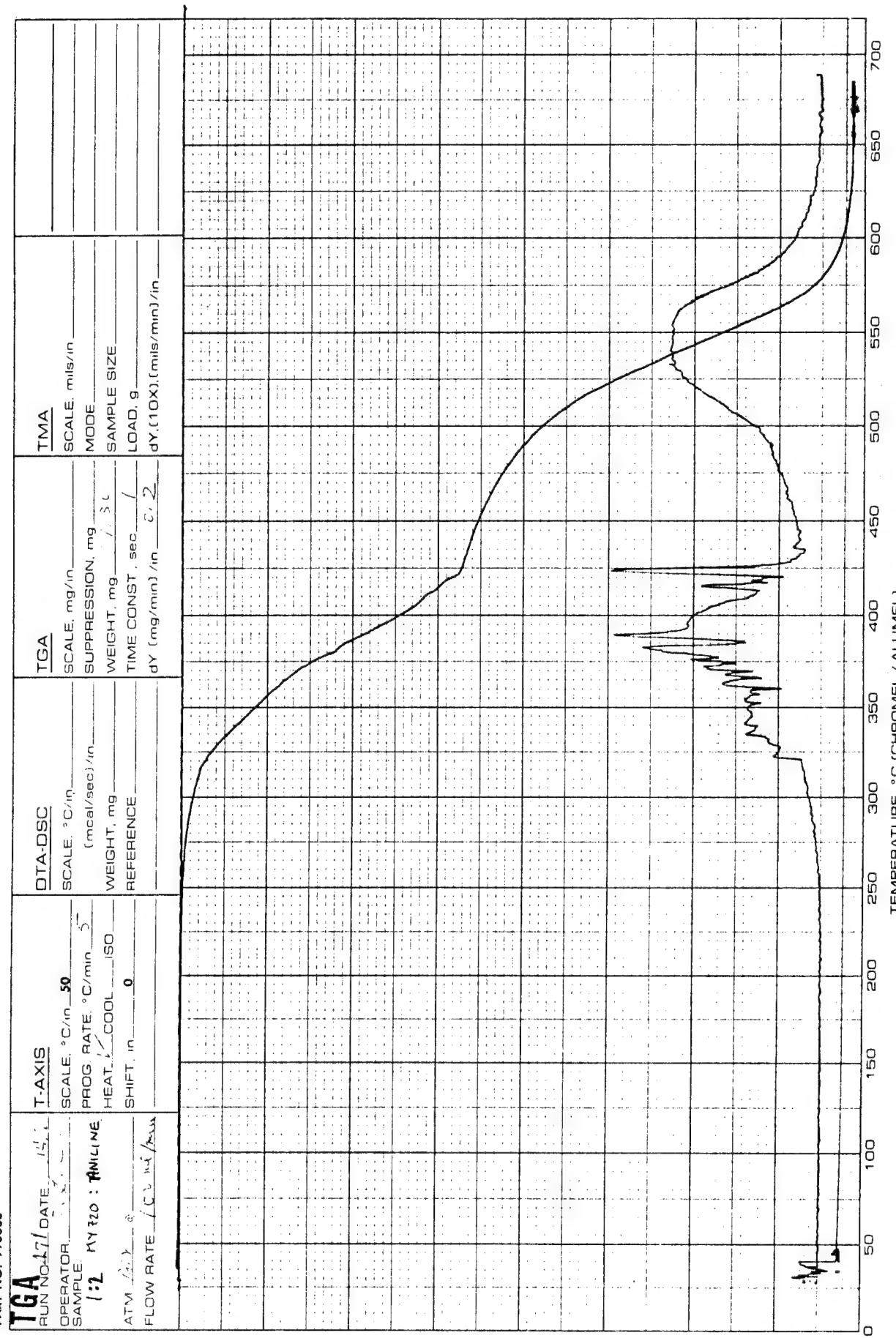


Figure 20: TGA of epoxy resin formed from 1:2 stoichiometric mixture of MY 720 and AN (in air)

PART NO. 9900088

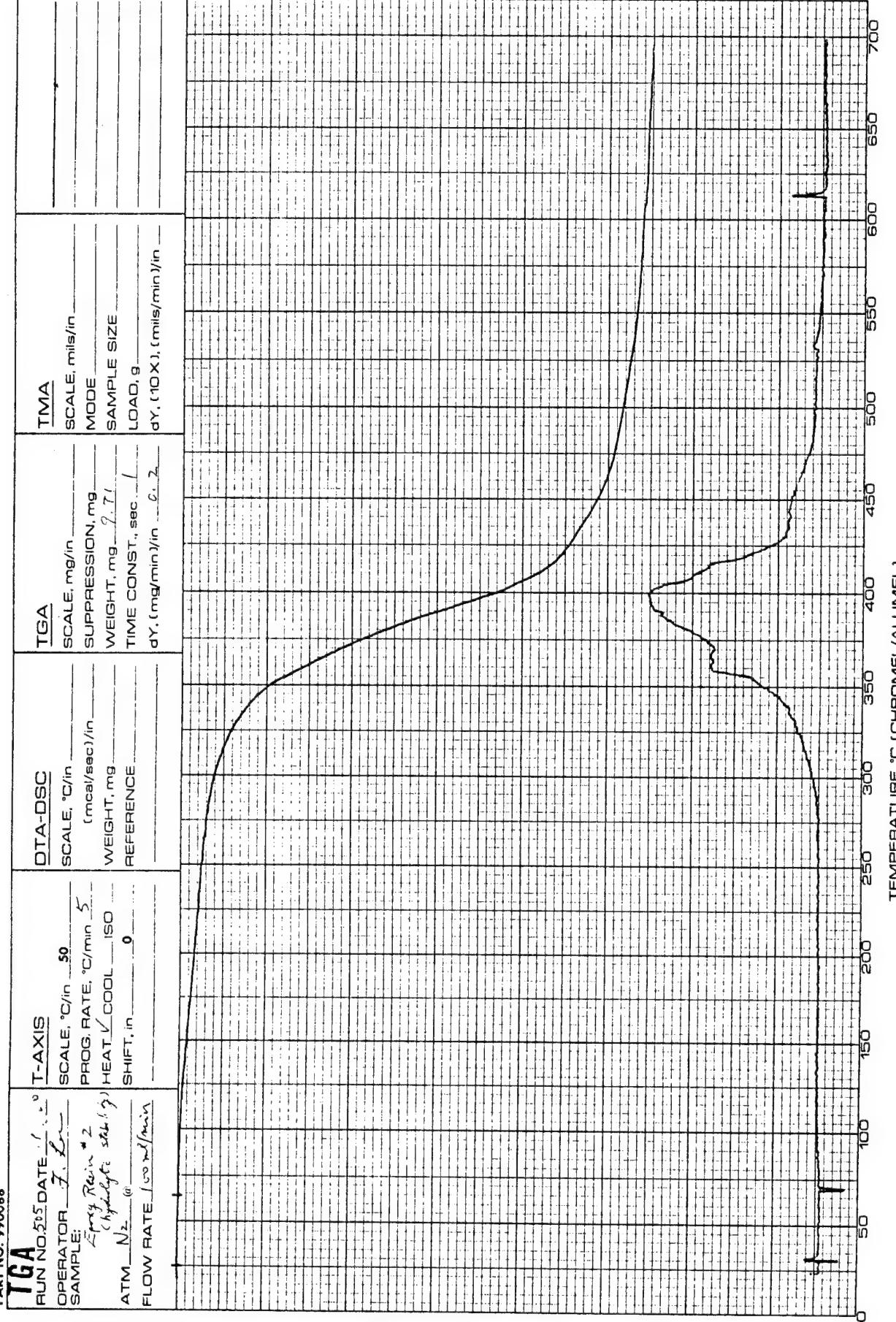


Figure 21: TGA of epoxy resin formed from 1 : 1 stoichiometric mixture of MY 720 and DAPS after exposure to 95% humidity (in nitrogen)

PART NO. 990088

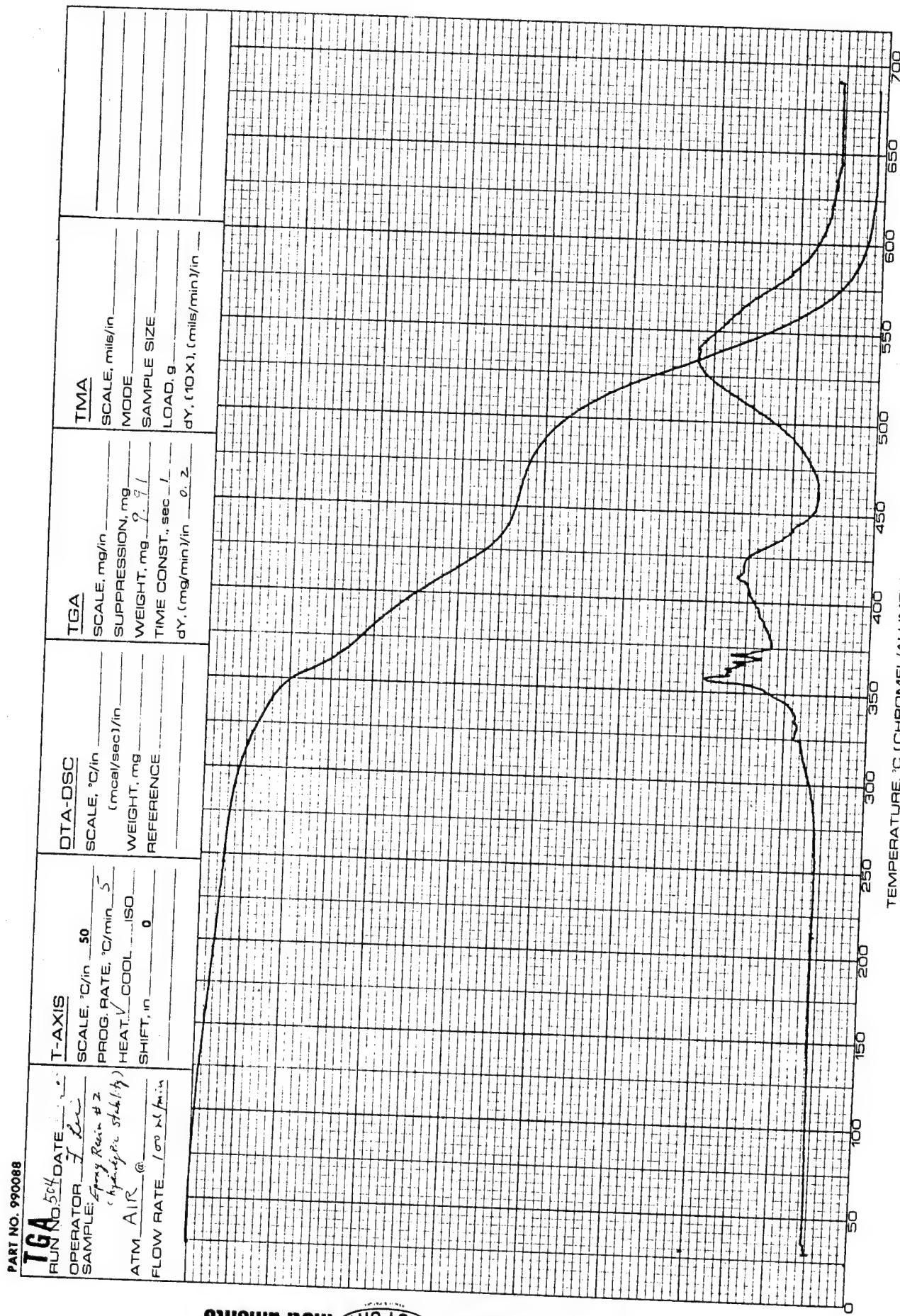


Figure 22: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and DAPS after exposure to 95% humidity (in air)

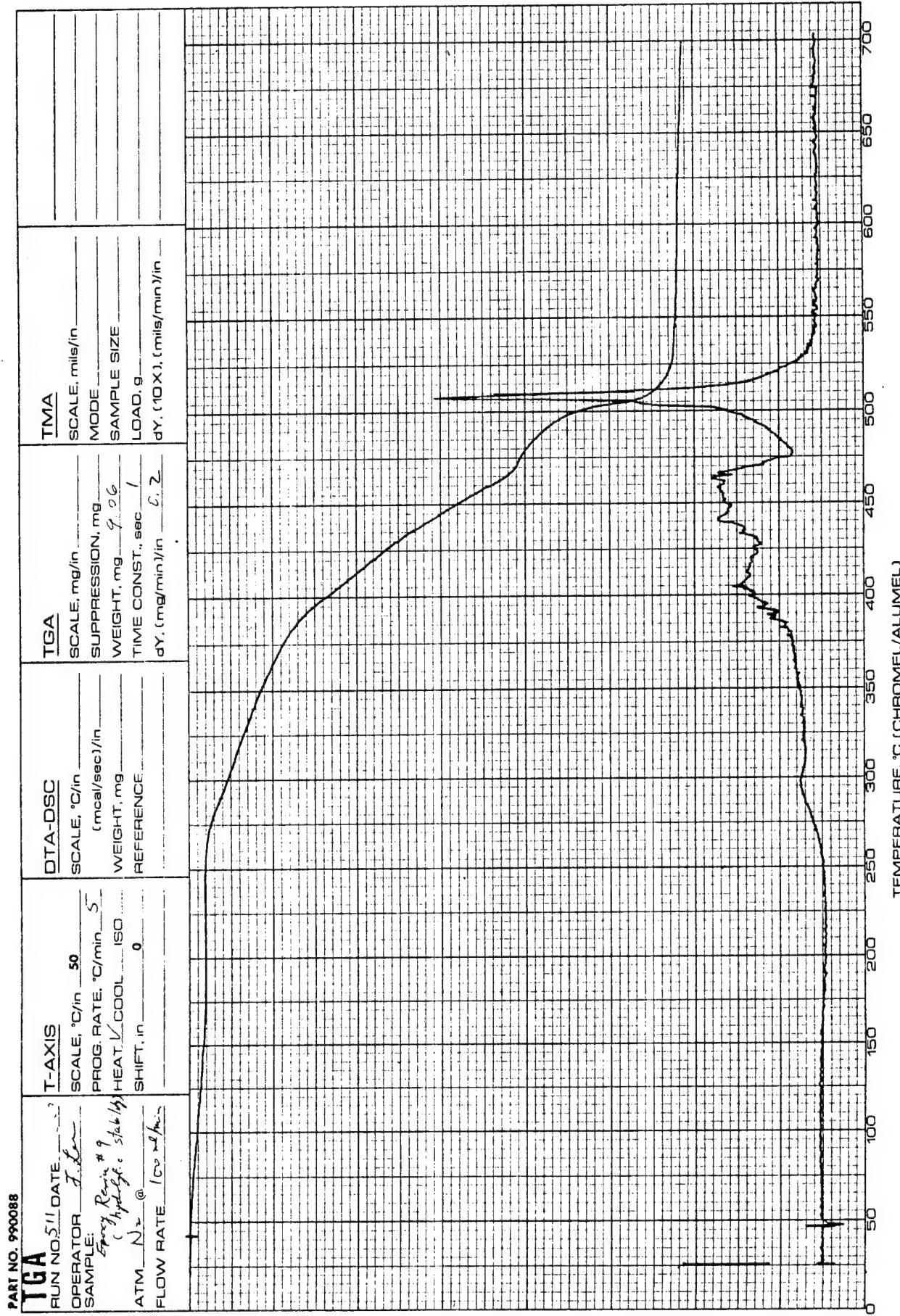


Figure 23: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PA after exposure to 95% humidity (in nitrogen)

PART NO. 990088

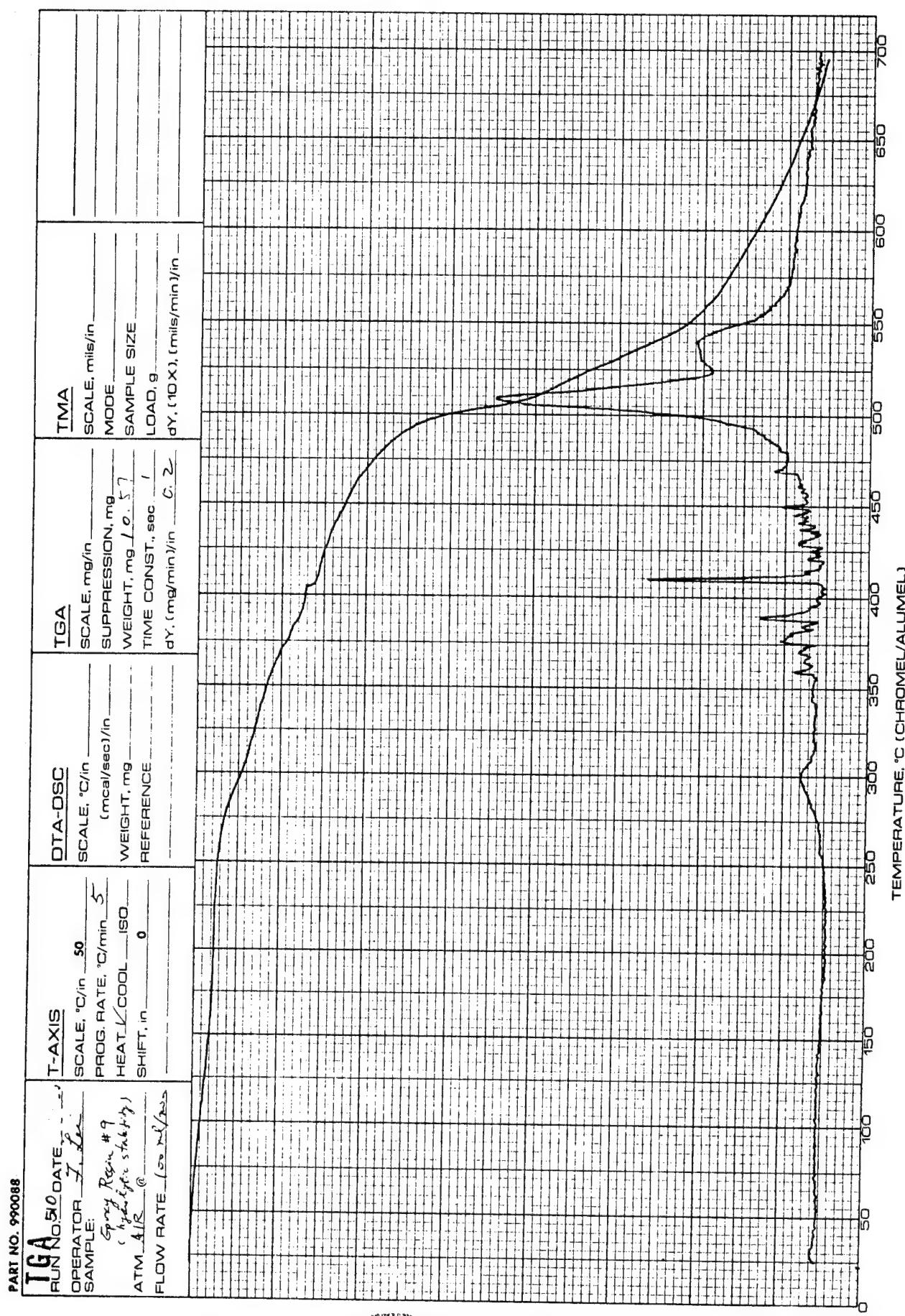


Figure 24: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PA after exposure to 95% humidity (in air)

PART NO. 990088

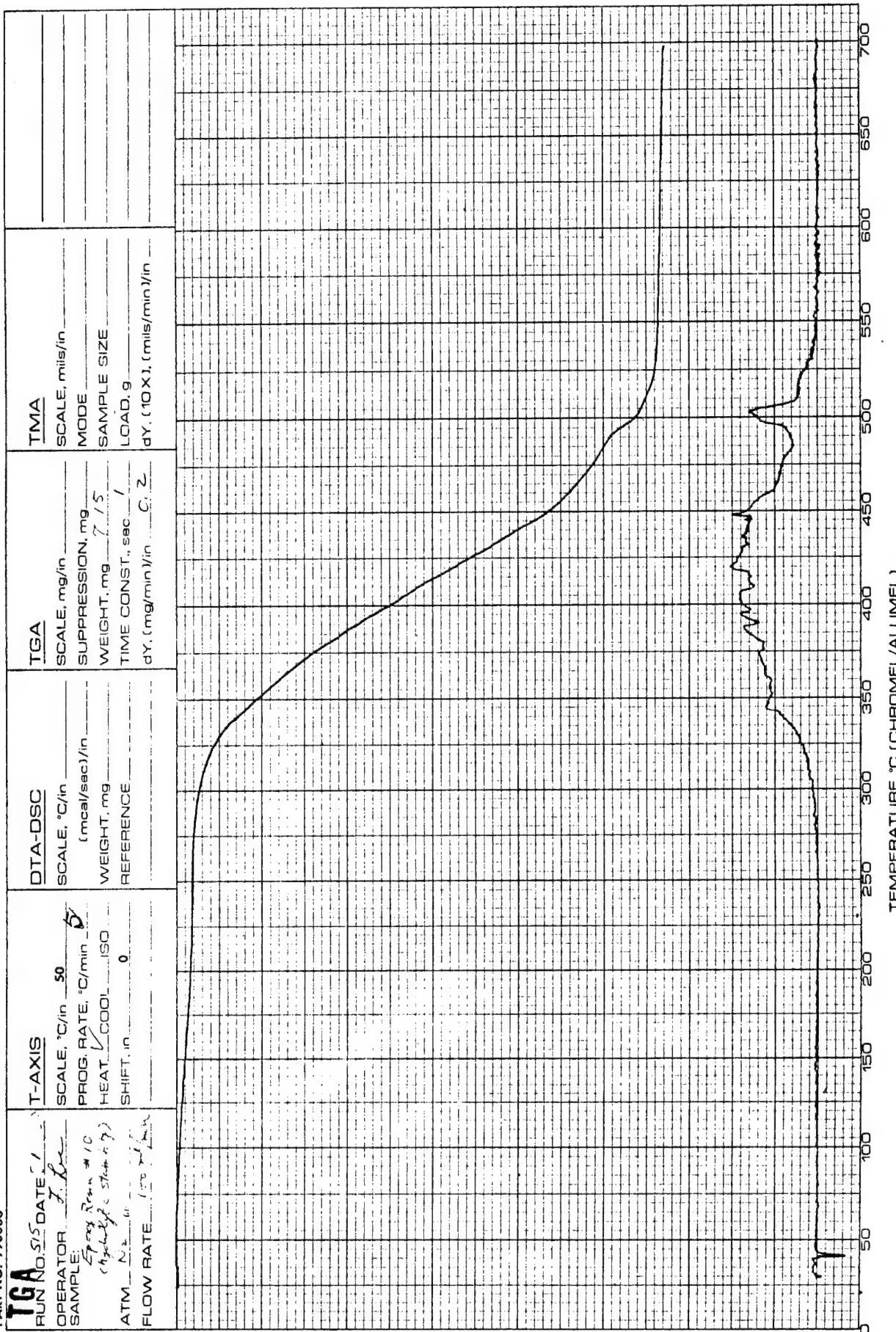


Figure 25: TGA of epoxy resin formed from 2 : 1 stoichiometric mixture of MY 720, DAPS, and PA after exposure to 95% humidity (in nitrogen)

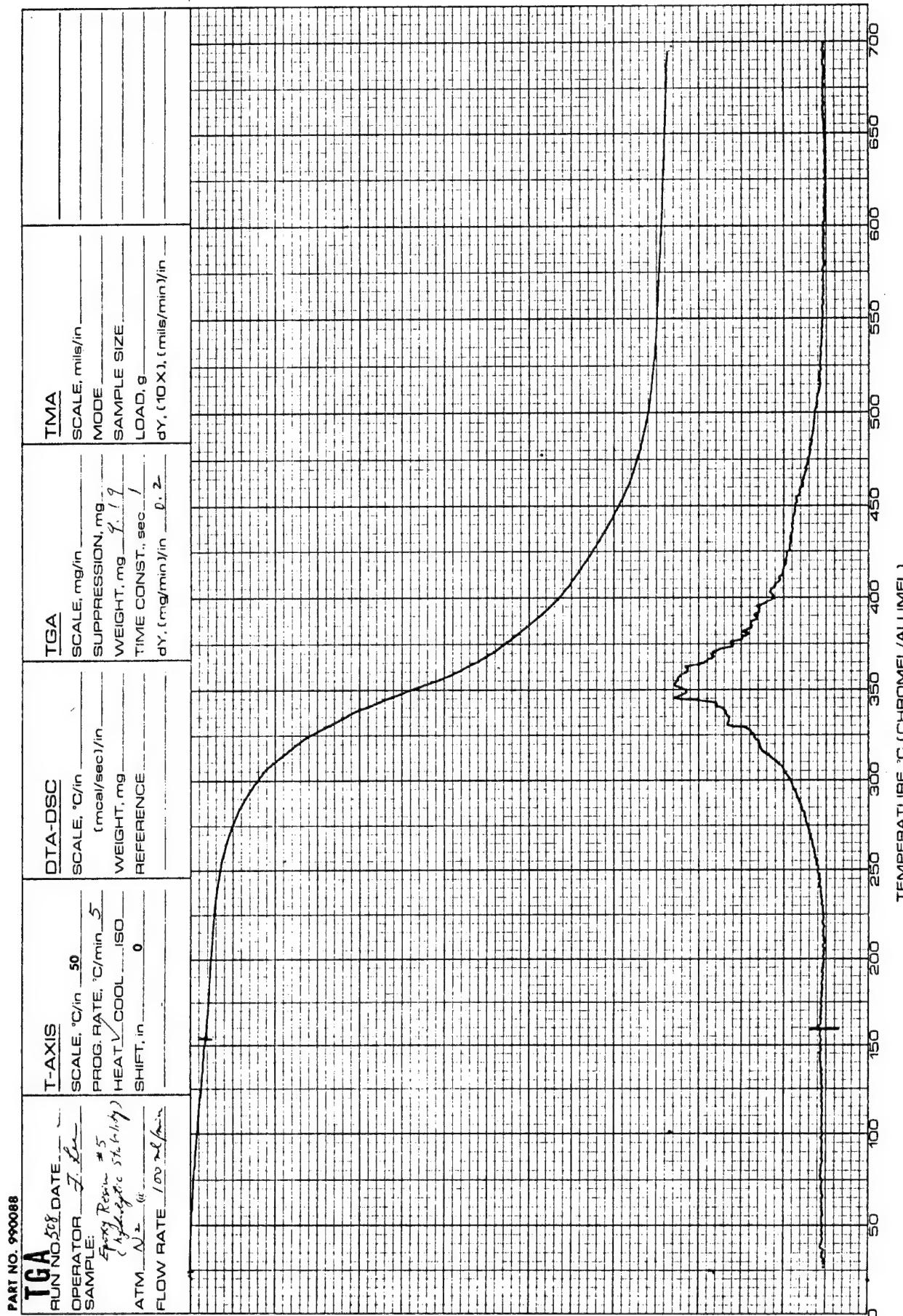


Figure 27: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PB after exposure to 95% humidity (in nitrogen)

PART NO. 9900086

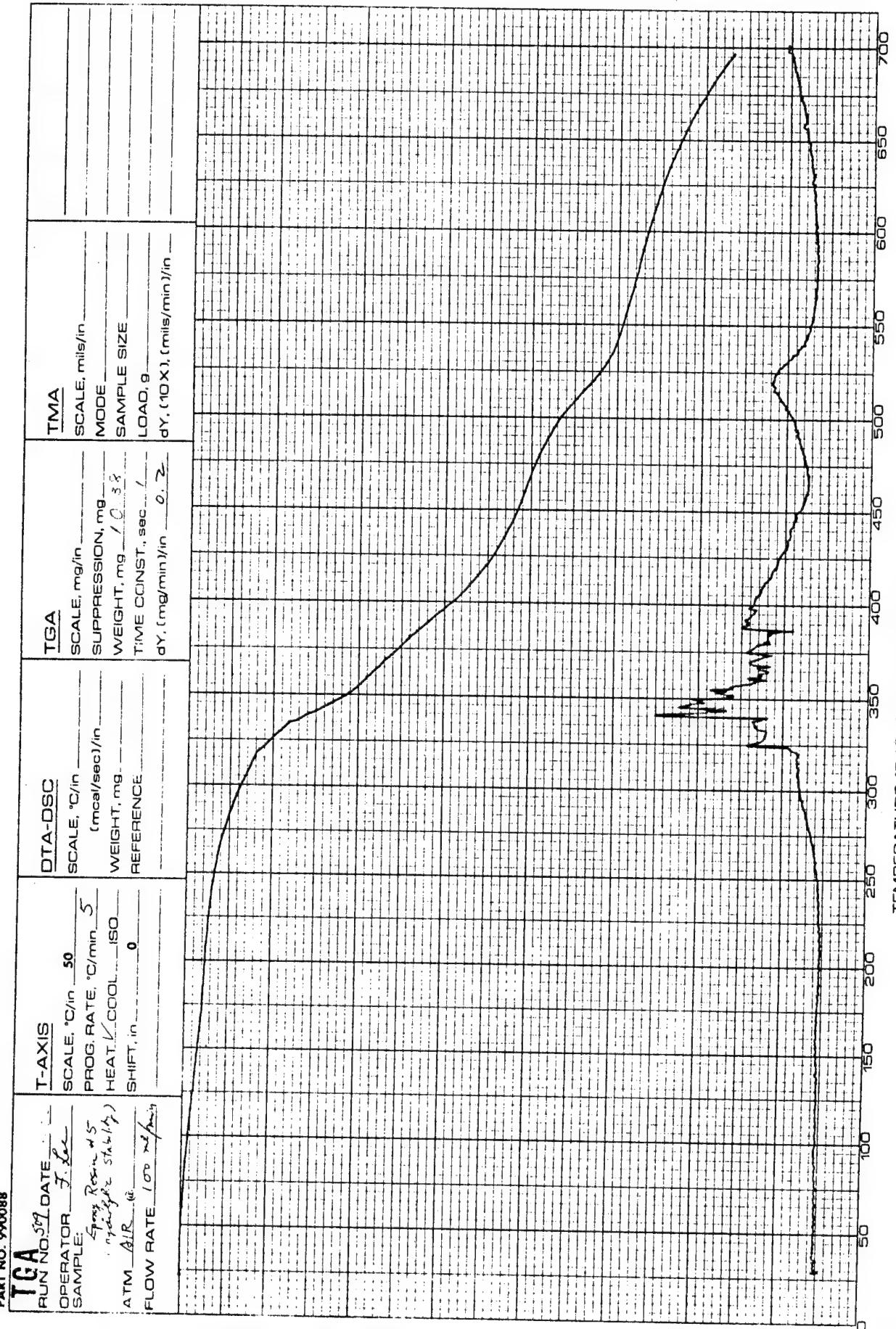


Figure 28: TGA of epoxy resin formed from 1:1 stoichiometric mixture of MY 720 and PB after exposure to 95% humidity (in air)

PART NO. 990088

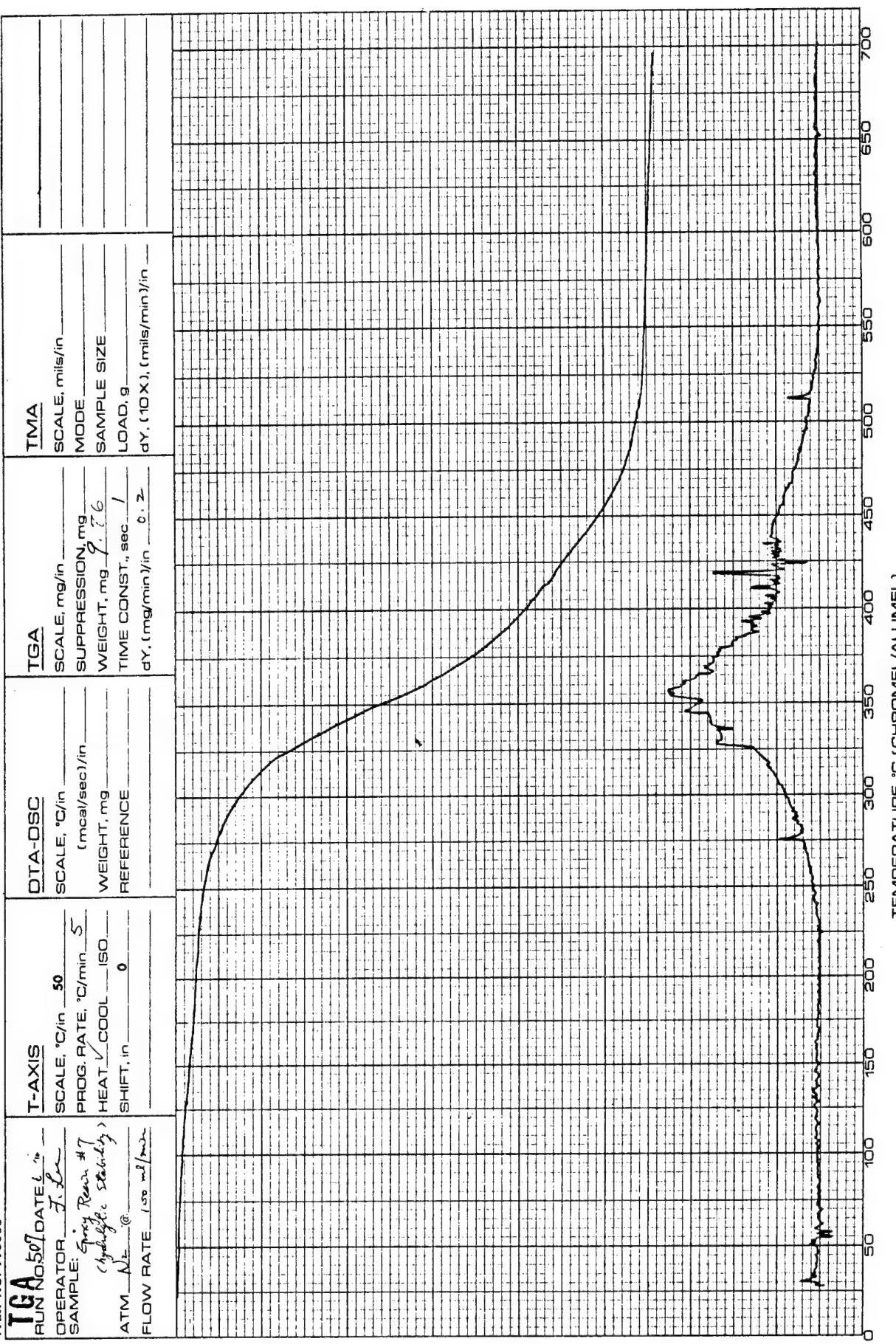


Figure 29: TGA of epoxy resin formed from 2 : 1 stoichiometric mixture of MY 720 and PB after exposure to 95% humidity (in nitrogen)

PART NO. 990088

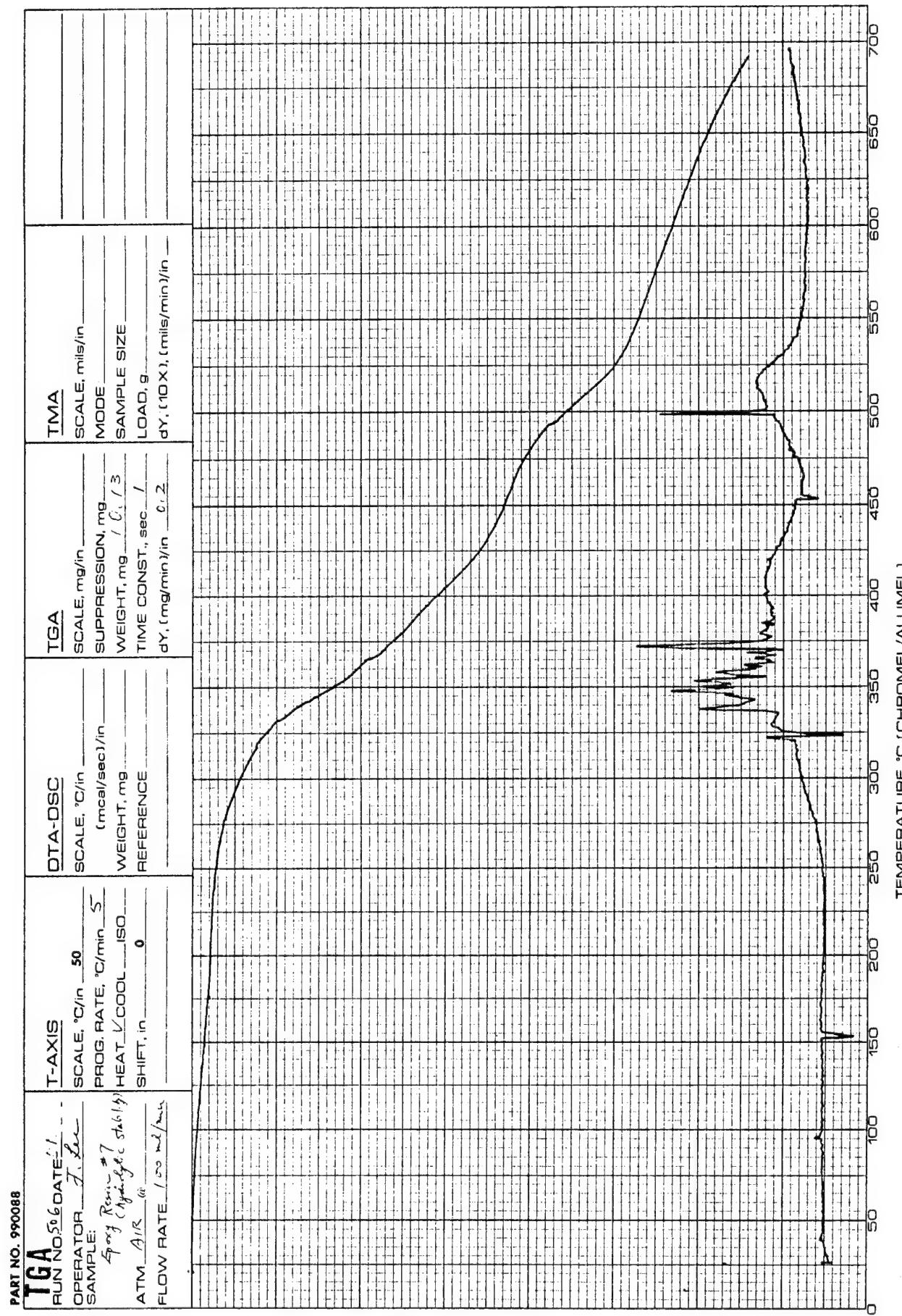


Figure 30: TGA of epoxy resin formed from 2 : 1 stoichiometric mixture of MY 720 and PB after exposure to 95% humidity (in air)

PART NO. 990088

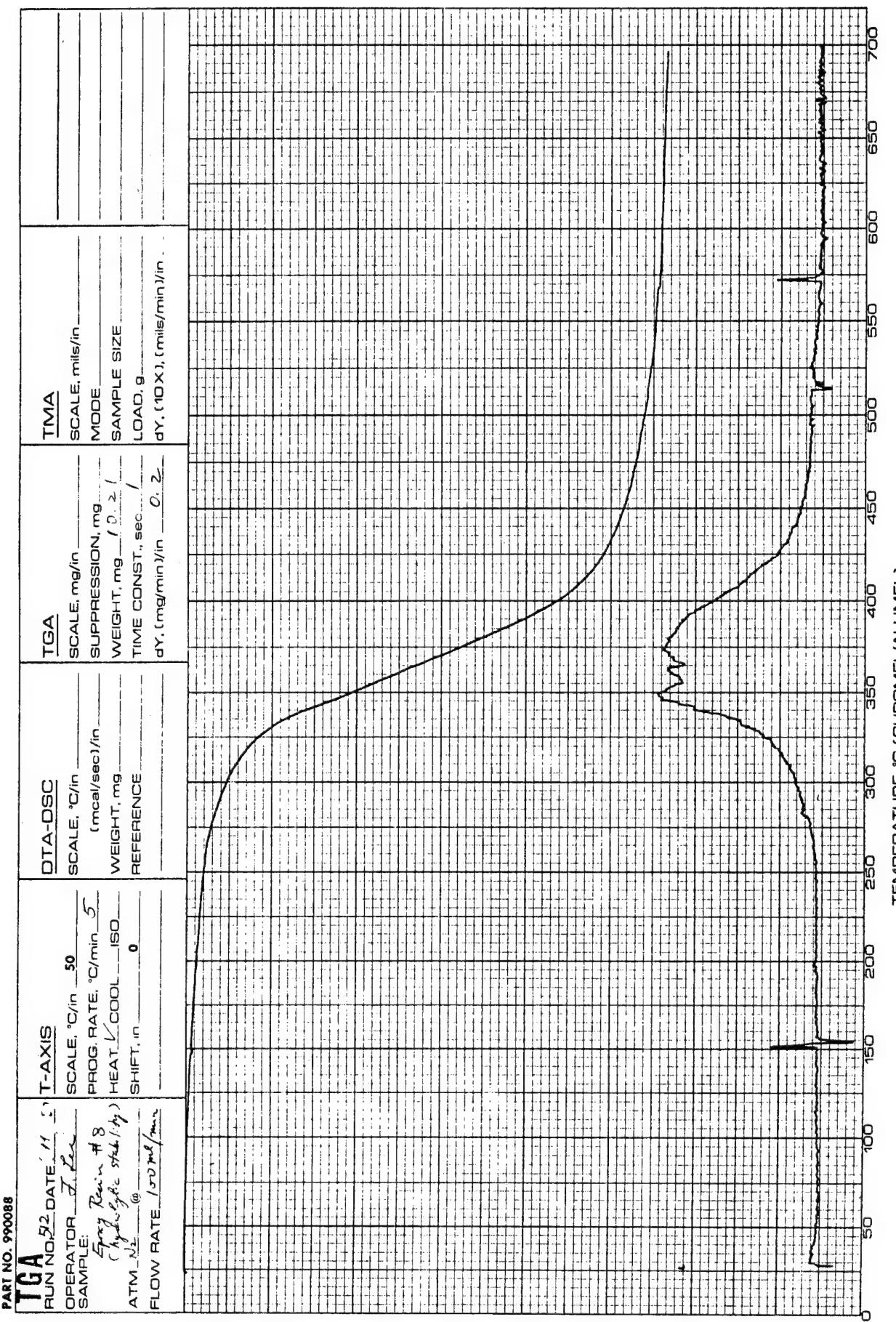


Figure 31: TGA of epoxy resin formed from 7 : 5 : 2 stoichiometric mixture of MY 720, DAPS, and PB after exposure to 95% humidity (in nitrogen)

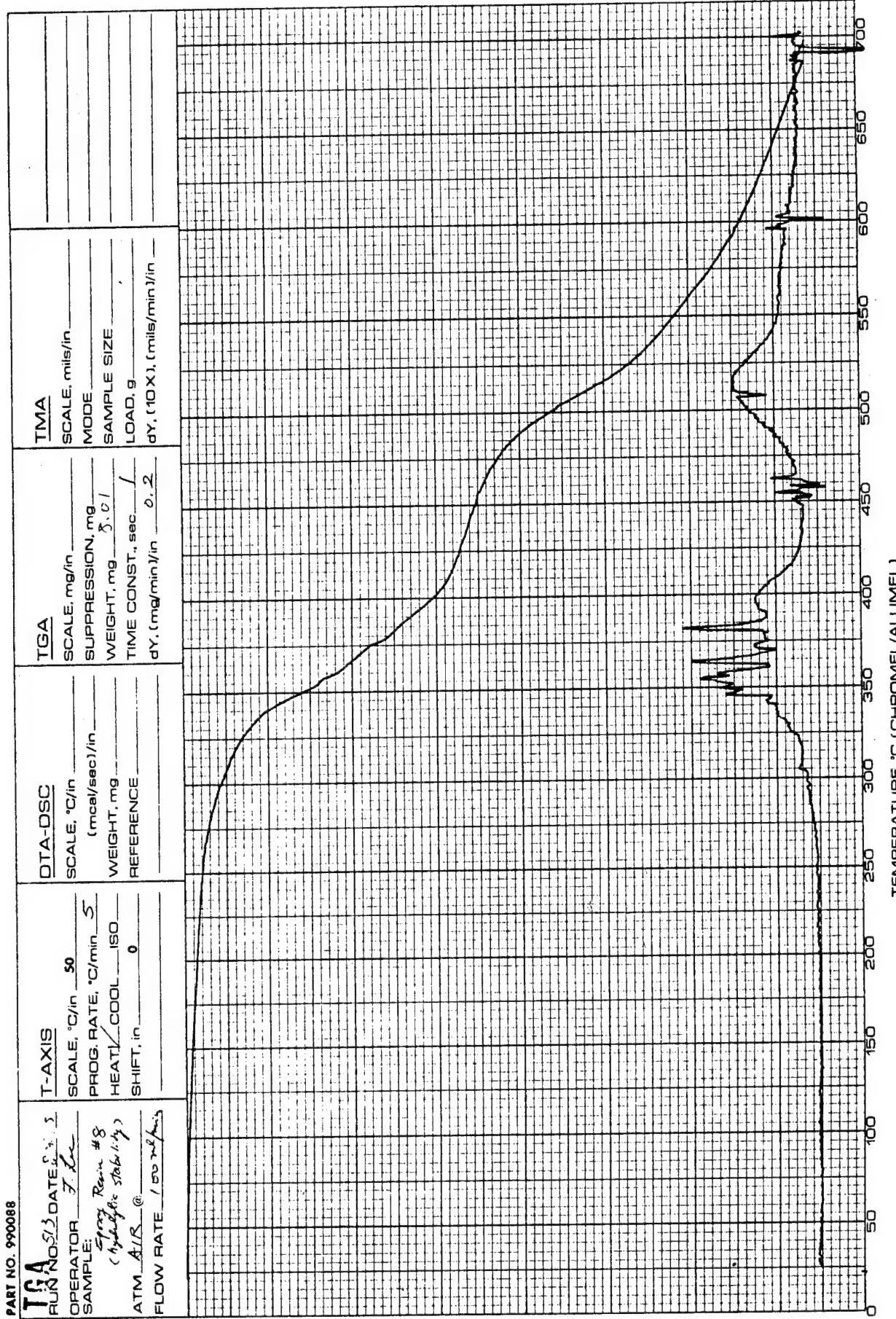


Figure 32: TGA of epoxy resin formed from 7 : 5 : 2 stoichiometric mixture of MY 720, DAPS, and PB after exposure to 95% humidity (in air)

PART NO. 990088

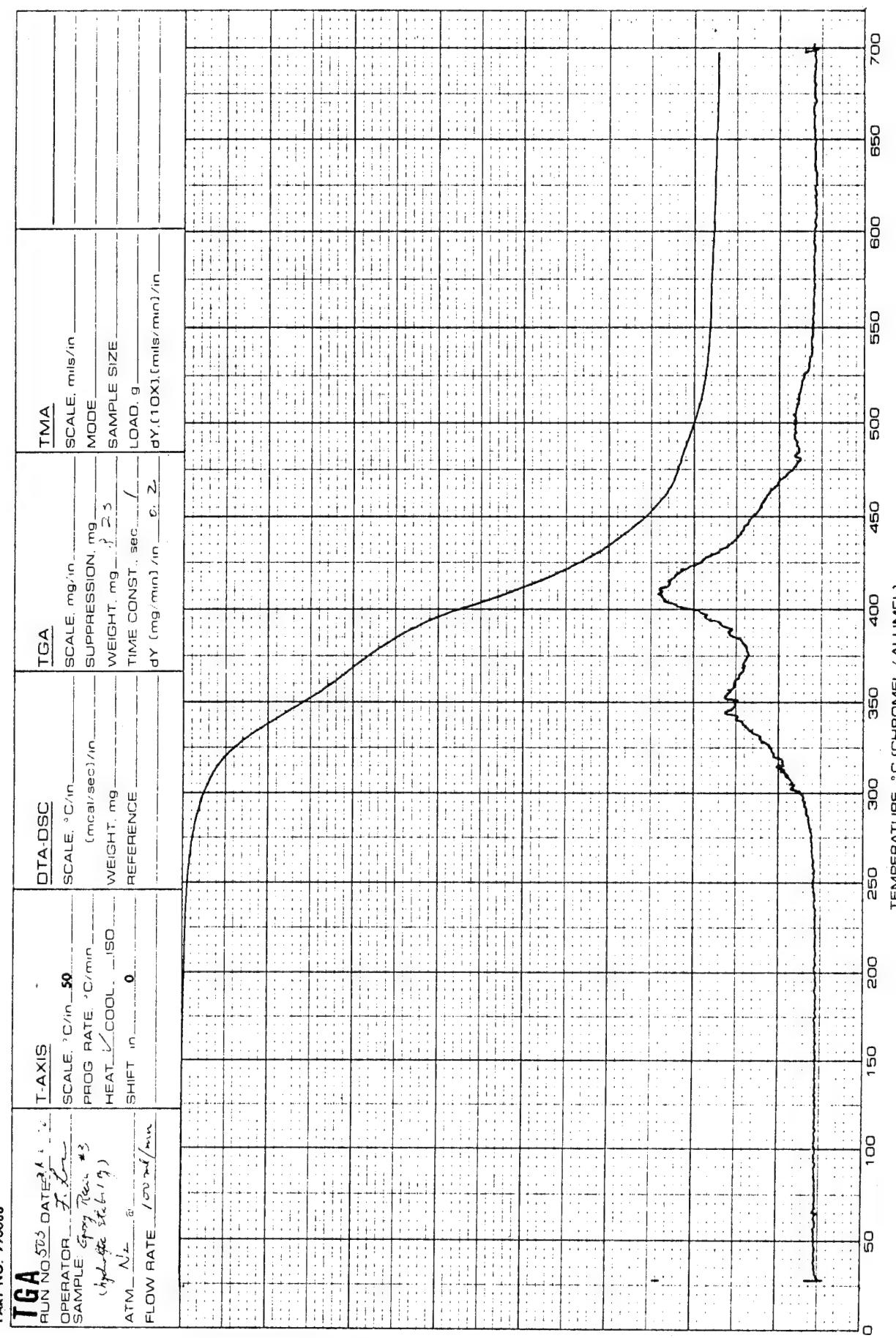


Figure 33: TGA of epoxy resin formed from 1:2 stoichiometric mixture of MY 720 and AN after exposure to 95% humidity (in nitrogen)

PART NO. 990088

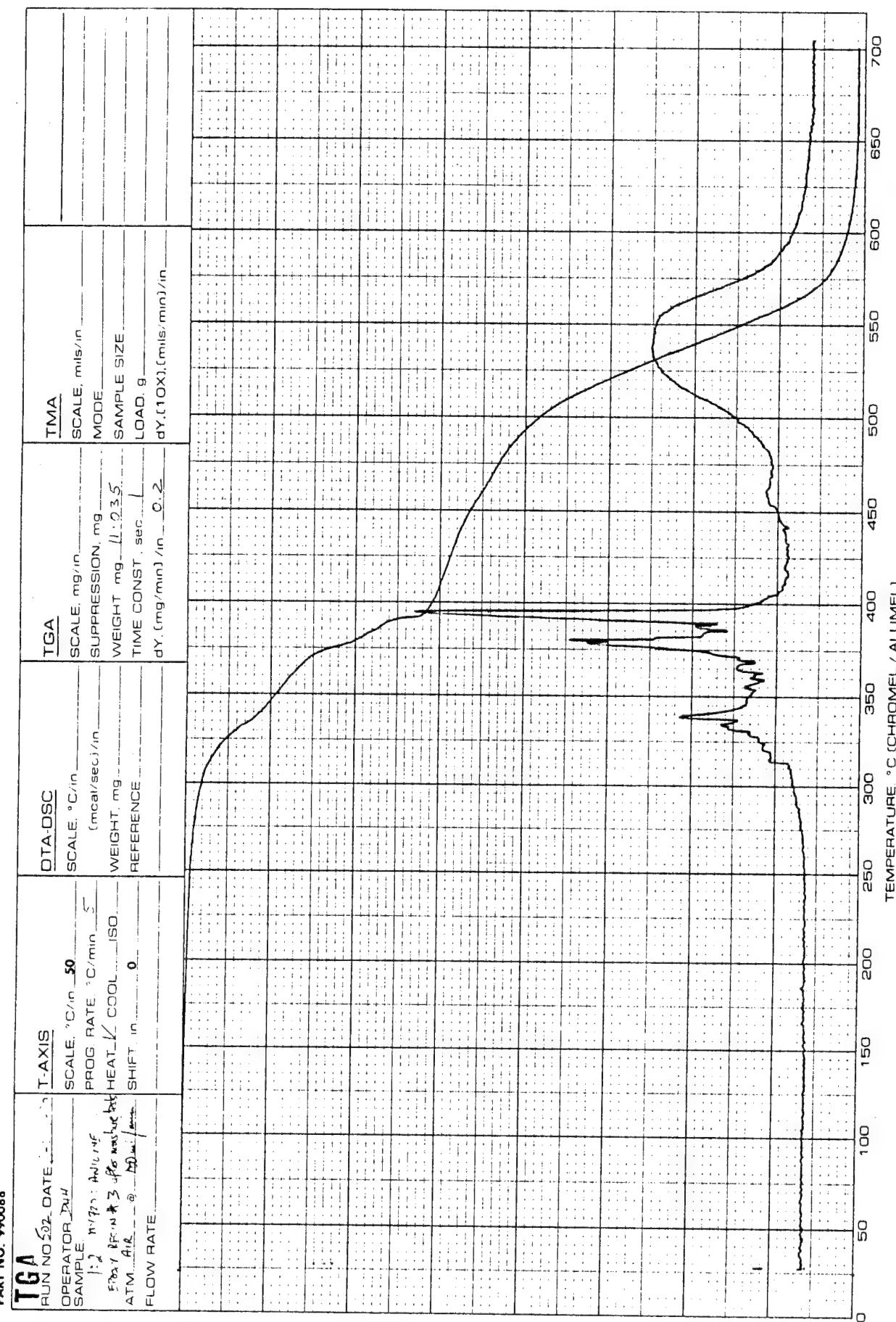


Figure 34: TGA of epoxy resin formed from 1:2 stoichiometric mixture of MY 720 and AN after exposure to 95% humidity (in air)

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